THEORETICAL AND APPLIED
ELECTROCHEMISTRY

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PREFACE TO THE FIRST EDITION

THE following book was written to supply a need felt by the author in giving a course of lectures on Applied Electrochemistry in the Massachusetts Institute of Technology. There has been no work in English covering this whole field, and students had either to rely on notes or refer to the sources from which this book is compiled. Neither of these methods of study is satisfactory, for notes cannot be well taken in a subject where illustrations are as important as they are here; and in going to the original sources too much time is required to sift out the essential part. It is believed that, by collecting in a single volume the material that would be comprised in a course aiming to give an account of the most important electrochemical industries, as well as the principal applications of electrochemistry in the laboratory, it will be possible to teach the subject much more satisfactorily.

The plan adopted in this book has been to discuss each subject from the theoretical and from the technical point of view separately. In the theoretical part a knowledge of theoretical chemistry is assumed.

Full references to the original sources have been made, so that every statement can be easily verified. It is thought that this will make this volume useful also as a reference book.

An appendix has been added, containing the more important constants that are needed in electrochemical calculations.

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PREFACE TO THE REVISED EDITION

In preparing a second edition of *Applied Electrochemistry* published in 1911, it was decided to include a treatise on theoretical electrochemistry as well, in accordance with suggestions received from a number of those who have used the first edition. This subject presupposes a general knowledge of physics and chemistry at least, and it would be desirable in addition to have had a course in physical chemistry, since electrochemistry is a branch of physical chemistry which is treated at greater length on account of its extensive application to industry. The object has been to include all the theory that would be of interest to an electrochemical engineer, without expanding the work to excessive length. The theory, Part I, can be covered in thirty hours of class-room work and the applied, Parts II and III, in thirty hours.

The works most extensively used as guides in preparing the theoretical discussion were Le Blanc's *Lehrbuch der Elektrochemie* (1922), and Foerster's *Elektrochemie wässeriger Lösungen* (1922), frequent references to which will be found in the text. Foerster's work is especially valuable for its very complete references. For the most recent developments in the ionic theory and the subject of the activities of electrolytes, Lewis and Randall's *Thermodynamics* has been of great assistance.

Part II, *Applied Electrochemistry of Aqueous Solutions*, and Part III, *Electric Furnaces and Their Products*, have been brought up to date and to a large extent rewritten.

The author wishes to thank Professors H. M. Goodwin and D. C. MacInnes of the Massachusetts Institute of Technology for criticisms of Part I; Mr. M. W. Merrill, Assistant Superintendent, Electrolytic Copper Refinery, United States Metals Refining Company, Chrome, N. J., for reading and criticizing Chapters VIII and X; Mr. Otis Hutchins, Metallurgical Engineer, The Carborundum Company, Niagara Falls, for criticizing Chapters XVII and XVIII, and Professor R. R. Lawrence of the Massachusetts Institute of Technology for assistance in preparing the discussion of induction furnaces.

Thanks are further due to the following persons for supplying valuable information: Mr. H. C. Bellinger, Vice President, Chili

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PART I

THEORETICAL
ELECTROCHEMISTRY
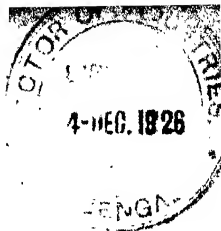
THEORETICAL AND APPLIED ELECTROCHEMISTRY

CHAPTER I

FARADAY'S LAW

Definitions. — Electrochemistry is that science which treats (1) of the chemical changes produced by the electric current, and (2) of the production of electricity from the energy of chemical reactions. Theoretically the two branches are equally important; practically, however, the chemical changes produced by the passage of electricity is much the more important of the two.

There are two classes of electric conductors, (1) those of the *first class*, metallic or electronic, in which the current is carried without the motion of matter, but by moving atoms of negative electricity called *electrons*, and (2) those of the *second class*, in which the current is carried by charged atoms or groups of atoms, called *ions*. This is called *electrolytic* conduction.

In general, conductors belong exclusively to one class or the other, but an exception to this has been found in solutions of the alkali metals in liquid ammonia. These form a connecting link between metallic and electrolytic conduction.[1] Very dilute solutions conduct electrolytically and as the concentration increases metallic conduction takes place simultaneously with electrolytic; finally, with concentrated solutions the conduction is entirely electronic. The explanation will be given later.

The principal cases in which electrolytic conduction takes place are in solutions and in fused salts, hydrates, and oxides. Chemical changes occur only when the current crosses the boundary between a first- and a second-class conductor; that is, at the *electrodes*, which are the conductors of the first class which lead the current to and

[1] Kraus, Tr. Am. Electroch. Soc. **21**, 119 (1912); J. Am. Chem. Soc. **43**, 2529 (1921).

3

from the electrolyte. The electrode which leads the positive current into an electrolytic cell is called the *anode*, while that which conducts the positive current from the cell is called the *cathode*.

Grotthuss' Theory. — The first satisfactory explanation of the fact that, in the electrolysis of water, hydrogen and oxygen appear only at the electrodes, was given by Grotthuss in 1805.[1] According to this, when the anode becomes positively and the cathode negatively charged by the application of a voltage to the cell, the electric forces between the electrodes and the negatively charged oxygen atoms and positively charged hydrogen atoms of water, then supposed to have the formula HO, caused all the molecules to turn so the oxygen faced toward the anode and the hydrogen toward the cathode, as in (*a*) Figure 1. If the attraction between the electrodes and the adjoining layer of atoms of opposite charge were sufficient, these would be liberated on the electrode and the atoms of opposite sign would be left behind (*b*). Those left behind would immediately combine with opposite atoms of neighboring molecules to form new molecules (*d*), which would then turn through 180 degrees so as to face in the same direction as before (*e*). This was supposed to take place instantly throughout the whole space between the electrodes so that for each hydrogen and oxygen atom liberated at the electrodes a complete chain of molecules between the electrodes break up, recombine, and turn through 180 degrees.

FIG. 1. — GROTTHUSS' THEORY OF ELECTROLYSIS

For about 50 years this was the accepted theory of electrolysis. It then became insufficient to explain the facts discovered during this time. It may be, however, that the Grotthuss chain action does take place to a certain extent, and would explain the abnormally high conductance of hydrogen and hydroxyl ions in aqueous

[1] Ostwald, Elektrochemie, p. 309 (1896).

solutions[1] and in general the high conductance of ions common with the solvent as has been found to be the case in solutions in pyridine, and in acetic, hydrobromic, and sulfuric acids.[2]

Faraday's Law. — The quantitative relation between the chemical change that takes place at each electrode and the amount of electricity producing the change was discovered by Faraday in 1834 and is expressed by **Faraday's Law of Electrolysis,** which may be stated as follows : *When a current passes across the junction between a purely metallic conductor and a purely electrolytic conductor, the quantity of chemical change produced, expressed in equivalents, is exactly proportional to the quantity of electricity which passes,* and is independent of everything else, such as temperature, concentration, current density, etc.[3] For example, a cell containing (1) silver nitrate with silver electrodes is connected in series with (2) a cell containing copper sulfate with copper electrodes, and (3) with a cell containing sodium chloride with platinum electrodes, and the same quantity of electricity is sent through each cell. Excluding secondary reactions, if a grams of silver are deposited at the cathode, a grams will be dissolved at the anode in cell (1); in cell (2), if b grams of copper are deposited at the cathode b grams will be dissolved at the anode, and if in cell (3) c grams of chlorine are liberated at the anode and d grams of hydrogen and e grams of sodium hydrate are produced at the cathode, the following relation will hold :

$$a : b : c : d : e = \frac{107.88}{1} : \frac{63.57}{2} : \frac{35.46}{1} : \frac{1.008}{1} : \frac{40.01}{1}.$$

Many careful measurements have been made to determine the number of coulombs necessary to decompose one chemical equivalent. These measurements consist in determining a quantity of electricity and the corresponding amount of chemical change. The chemical change nearly always selected is the deposition of silver from a neutral silver nitrate solution, as this is subject to less errors than nearly any other reaction. The quantity of electricity is measured by holding the current passing the cell constant for a measured time. The errors in the time measurement are negligible. The current must be measured by a primary

[1] Danneel, Z. Elektroch. **11**, 249 (1905).
[2] Hantzsch and Caldwell, Z. phys. Ch. **58**, 575 (1907).
[3] Experimental Researches, Vol. 1, Series III, § 8, p. 102, and Series VII, § 11, p. 195. The statement of this law is given by Faraday in the form of two distinct laws.

instrument whose constants can be computed from its dimensions, such as a tangent galvanometer, electrodynamometer, or current balance. The accuracy of these instruments depends on the accuracy with which their constants are known; for the tangent galvanometer this depends on the accuracy of the horizontal component of the earth's magnetism, and for current balances on the accuracy of the acceleration due to gravity at the place where the measurements are made. The mean value of a large number of determinations made at the Bureau of Standards is that one coulomb deposits 1.1180 milligrams of silver.[1] This is called the electro-chemical equivalent of silver. Taking the atomic weight of silver as 107.88, the faraday, the number of coulombs required to deposit one equivalent, is $F = 107.88/0.0011180 = 96,494$. This is also called the electro-chemical constant. The value 96,540 adopted by the International Congress of Applied Chemistry of 1903 is based on the atomic weight of silver = 107.93 and on the definition of the legal ampere, which in one second deposits 0.001118 g. of silver.[2] The value 96,500 will be adopted in this work. A table of electro-chemical equivalents will be found in the appendix.

Coulometers. — It is evident from the above that the amount of electricity passing through a circuit can be determined from the amount of chemical change produced at any electrode if this chemical change can be measured. There are three general methods of making this measurement: (1) by weighing the substance deposited or liberated, (2) by measuring its volume, and (3) by titration. It seems hardly necessary to call attention to the fact that in any coulometer the current can be computed from the quantity of electricity that has passed through the circuit, if the current has been constant and if the time is measured. Current in amperes equals quantity in coulombs divided by time in seconds.

The errors of coulometers are those inherent in the measurement of weight and volume or in titration, and also those due to imperfections in the coulometer itself. The latter may come from a variety of causes, such as the liberation of other substances than the one assumed, or the loss of the substance after deposition and before weighing. The errors of each coulometer described below will be pointed out.

[1] Bull. Bureau of Standards, 1, 363 (1905); and Scientific Paper No. 285 (1916).
[2] See appendix.

The *silver coulometer* is the most accurate of all coulometers. The specifications [1] for the use of this coulometer proposed by the Bureau of Standards are the following. These are intended for an accuracy of 0.001 percent, and for this accuracy the result should be the mean of several separate experiments with two or more coulometers in series.

For work requiring 0.01 percent accuracy the precautions may be somewhat reduced though the mean of several deposits should be taken. The labor of weighing the deposits and purifying the salt may be considerably lessened, provided the unpurified electrolyte does not contain more than 25 parts of acid in 1,000,000 or enough alkali to produce striation. No observations should be used in which the deposits show striation.

For work requiring 0.1 percent accuracy, the c. p. silver nitrate prepared by the best manufacturing chemists may be used without purification. A small amount of filter paper may be used to separate anode and cathode. This will cause striation, but deposits showing excessive striations of leaden color should not be relied on. With careful manipulation the mean of two deposits should give results of the desired accuracy.

Specifications —

1. The electrolyte shall consist of 10 to 20 g. of silver nitrate in 100 cc. of solution made with water having a specific conductance of not more than 2×10^{-6} mho per centimeter cube.

2. The electrolyte must be free from organic or other reducing substances and from colloids. Reducing substances are tested for chemically by adding 0.001-n-KMnO$_4$ solution 1 cc. at a time to 10 cc. of 66 percent solution of the AgNO$_3$ acidified until the color persists for 5 minutes. (See Vol. 9, p. 531.) The crystalline deposit must be free from striations, and the same weight of deposit should be given by a small and by a large coulometer. Heavier deposits are obtained in large rather than in small coulometers if reducing impurities are present.

3. The silver nitrate may be purified by crystallization from acid solution and by fusion. If the chemical test for purity is omitted, it should be purified until further crystallization from acid solution and subsequent fusion does not change the weight of the deposit. Before making up the solution the surface of the fused cake should be washed.

4. The coulometer should not contain less than 75 cc. in the cathode chamber, and the deposit should not reduce the concentration in the cathode compartment below 5 percent.

5. The electrolyte must be neutral or slightly acid as tested by methyl red or iodeosin. As one part in 1,000,000 of base may increase the deposit

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[1] Rosa and Vinal, Bull. Bureau of Standards, **13**, 479 (1916).

appreciably it may be better to have an acidity of one part in 1,000,000 than to risk a slight basicity in trying to make strictly neutral. Any diaphragm material which makes the electrolyte basic or produces more than a trace of acid must be avoided.

6. The most convenient form of cathode is that of a bowl or crucible preferably of platinum, but gold, which is less durable, may be used. The capacity should be from 125 to 400 cc. The form used by Richards, Collins, and Heimrod is shown in Figure 2.[1] The porous cup of Pukall ware, made by John Maddock of Trenton, N. J., is to prevent anode mud from dropping on the cathode, and the level of the liquid in the cup is below that outside, in order to cause a flow in the direction opposite to Ag_3^+ ions, which would cause a deposit of too much silver if they reached the cathode.

Fig. 2. — POROUS CUP COULOMETER

The surface of the cathode should be smooth and bright, and the deposit should be removed by acid or by electrolysis. The current density should not exceed 1 amp./sq. dm. The current should be constant and not more than 1 ampere and the time not less than 1 hour.

7. The anode should be of pure silver and is preferably coated with electrolytic silver. It should be heated to 200° before used to remove any acid coming from the solution. Its size should be as large as the cathode permits.

8. After thorough washing, the cathodes are dried at 150°, and weighed. The weight of silver is reduced to vacuo.

Pure distilled water should be used for washing, and may be tested with KBr for $AgNO_3$, or the conductivity may be determined and compared with its initial conductivity. Five to seven washings are usual, and they should be done without delay. It is not desirable to soak the deposits in water overnight.

[1] Proc. Am. Acad. **37**, 415 (1902).

FIG. 3. — COPPER COULOMETER

The *copper coulometer* consists usually of two sheets of copper for anodes, with a thin copper sheet hung between them as cathode, in an acid solution of copper sulfate. It is not so accurate as the silver coulometer for several reasons. In the first place, only 0.29 gram copper is deposited to every gram of silver. This reduces the percentage accuracy of the weight to about one third of the value it would have for an equivalent amount of silver. More important than this are the chemical reactions that tend to change the weight of copper deposited on the cathode from the correct weight. The copper cathode dissolves slightly in acid cupric sulfate, in the presence of oxygen :

$$Cu + O + H_2SO_4 = CuSO_4 + H_2O,$$
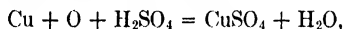
thereby reducing the weight of the cathode. On the other hand, in a neutral solution the plate gains in weight, due to a covering of cuprous oxide coming from hydrolysis of the cuprous sulfate.

The solution generally used in the copper coulometer is that recommended by Oettel,[1] consisting of 1000 grams of water, 150 grams of crystallized copper sulfate, 50 grams of concentrated sulfuric acid, and 50 grams of alcohol. For ordinary purposes the exclusion of air is not necessary. The current density on the cathode should lie between 2 and 20 milliamperes per square centimeter. The advantages of the copper over the silver coulometer are its greater cheapness and the greater adhesiveness of the deposit on the cathode. The average error of a single determination is from 0.1 to 0.3 percent.[2] A convenient form of the copper coulometer is shown in Figure 3. The inside dimensions of the glass vessel are approximately 4.3 centimeters in width, 16 centimeters in height, and 17 centimeters in length.

The *water coulometer* measures the quantity of electricity passing through a circuit by the amount of water decomposed between unattackable electrodes dipping in a solution through which the current flows. The amount of water decomposed may be determined by measuring the loss in weight of the coulometer, by measuring the total volume of gas produced, or by measuring the volume of either one of the gases separately.

The decomposition of water by the electric current was first observed by Nicholson and Carlisle [3] in 1800. In 1854 Bunsen [4]

[1] Chem. Zeitung, **17**, 543 and 577 (1893).
[2] Ostwald-Luther, *Hand- und Hülfsbuch*, 3d ed. 497 (1920).
[3] Gilbert's Ann. **6**, 340 (1800).
[4] Pogg. Ann. **91**, 620 (1854).

used a water coulometer in which the loss in weight was determined; and since then others have devised coulometers on the same principle.[1] Figure 4 shows a convenient form of the apparatus, having a drying tube sealed directly to it; for before leaving the cell the gases must, of course, be thoroughly dried so that no water vapor is carried off with them. It is evident that this instrument cannot give great accuracy on account of the relatively small change in weight produced by the passage of an amount of electricity equal to the electrochemical constant. In the case of water the change in weight is only 9 grams, as compared with 31.2 grams of copper and 107.9 grams of silver. The errors inherent in the instrument itself are due to the formation of other products than hydrogen and oxygen. If a solution of sulfuric acid is used between platinum electrodes, the oxygen liberated on the anode contains a certain amount of ozone.[2] Persulfuric acid, $H_2S_2O_8$, and hydrogen peroxide, due to the oxidation of water by the persulfuric acid, are also produced. The production of persulfuric acid is a maximum when the concentration of the solution is between 30 and 50 grams of sulfuric acid to 100 grams of water.[3] For this reason a 10 to 20 percent solution of sodium hydrate is often used, in which none of the above disturbing reactions occur.

Fig. 4.—WATER COULOMETER

(labels: Cotton, Calcium Chloride, Glass wool, Sealed Joint)

The presence of even a small amount of salt of a metal with two different valences, such as iron, may cause a very large error.

The *silver titration coulometer* of Kistiakowsky[4] is sometimes convenient where the current does not exceed 0.2 ampere and
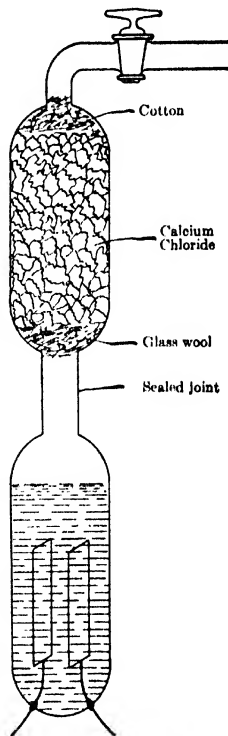
[1] L. N. Ledingham, Chem. News, **49**, 85 (1884).
[2] Schönbein, Pogg. Ann. **50**, 616 (1840).
[3] Franz Richarz, Ann. d. Phys. **24**, 183 (1885); **31**, 912 (1887).
[4] Z. f. Elektroch. **12**, 713 (1906).

where the duration of the experiment does not exceed an hour. A silver anode is dissolved in a 10 percent potassium nitrate solution by the passage of the current, and the solution is then titrated. In the form shown a silver anode is at the bottom in the nitrate solution with which the tube is $\frac{3}{4}$ filled. Then $\frac{1}{2}$ to $\frac{1}{4}$ normal nitric acid is carefully poured on top of the nitrate solution and a platinum cathode is immersed in the acid. After the experiment the potassium nitrate solution containing the dissolved silver is drawn off and titrated with 0.02 normal potassium thiocyanate, and a saturated iron alum solution as indicator. The error of a single determination may amount to 0.5 percent.

The *iodine coulometer*,[1] in which the iodine, set free at the anode by the passage of the current through a potassium iodide solution containing iodine, is titrated, has been found comparable in accuracy with the silver coulometer. This reaction is completely reversible, so that the free iodine reduced at the cathode to iodide may be used as a check on the amount set free at the anode. Of course the anode and cathode compartments must be completely separated so that no mixing of their contents can take place.

When coulometers are used for commercial purposes they are called *electrolytic meters*. At the beginning of electric lighting the Edison meter, consisting of zinc electrodes in a zinc sulfate solution, was used. The quantity of electricity was determined by the loss in weight of the anode. Many other technical meters have been devised, but they are of no importance in this country.[2]

Fig. 5. — Kistia-
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lometer
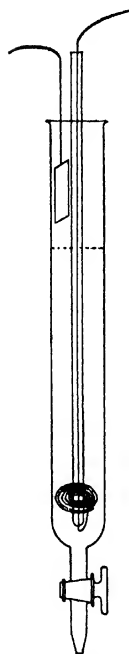
Current Efficiency. — It does not necessarily follow from Faraday's law that in an electrolysis 100 percent of the amount of product calculated will actually be obtained. Secondary effects may prevent this. For example, in copper refining an appreciable amount of copper is redissolved by the action of the air and sulfuric acid, and in nickel plating hydrogen is deposited with the nickel.

[1] Washburn and Bates, J. Am. Ch. Soc. **34**, 1341 (1912); Vinal and Bates, Bull. Bureau of Standards, **10**, 425 (1914).
[2] See Norden, *Elektrolytische Zäler* (1908).

Consequently in these and similar cases only part of the copper or nickel calculated from Faraday's law is obtained. The ratio of that obtained to the theoretical amount is called the *current efficiency*, and is usually expressed in percent.

Current Density. — The current divided by the area of the electrode is called *current density*, and is usually expressed in amperes per square decimeter or per square foot.

Current Concentration. — The current divided by the volume on which the current acts is called the *current concentration*. A high value of this quantity is desirable if a high concentration is to be produced of some compound subject to chemical decomposition.[1]

FIG. 6. — SERIES ELECTRODES

Intermediate Electrodes. — When an electrode is placed between the electrodes connected to the source of electricity so that a part or the whole of the current must pass through it, this is called an *intermediate electrode*. The face toward the anode is a cathode, and that towards the cathode is an anode. Any number of electrodes may be so placed as shown in *C* to *G* in Figure 6. Intermediate electrodes are used in the series system of copper refining.
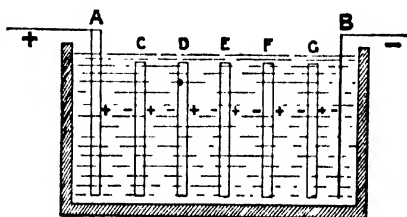
Multiple or Parallel Connection applies to electrodes when every alternate electrode is connected to one terminal of the current supply and the remaining electrodes to the other, as shown in Figure 7.
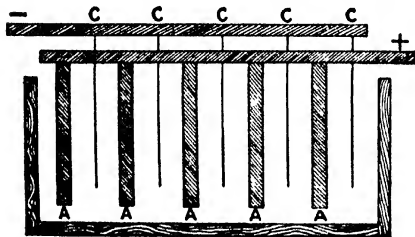
FIG. 7. — MULTIPLE CONNECTION

Nomenclature. — It is evident from Faraday's law that in a solution of an electrolyte a definite quantity of electricity, a *faraday*, must be combined with one equivalent of atoms or radicals. These

[1] Tafel, B. B. **33**, 2212 (1900).

combinations of atoms or radicals with electricity are the ions referred to above. It is their motion through the solution which constitutes the current. From the fact that some are deposited on the cathode and some on the anode, it follows that some ions have positive and others negative charges. Those ions with positive charges are deposited on the cathode, and are called *cations*, those with negative charges on the anode, and are called *anions*. Thus in electrolyzing a solution of nickel chloride, nickel deposits on the cathode and chlorine on the anode. Chlorine is therefore combined with negative and nickel with positive electricity. In general, in solution the metals and hydrogen possess positive charges, forming cations, while the halogens and all acid radicals possess negative charges, forming anions.

Avogadro's Number. — The number of positive charges of a cation is due to the number of electrons lost, and the number of negative charges gained by anions is due to the number of electrons gained by the atom or radical in question. If N is the Avogadro number, that is, the number of atoms in one atomic weight of any element $(= 6.06 \times 10^{23})$, and e the elementary charge of electricity carried by one electron $(= 1.59 \times 10^{-19}$ coulomb), then the faraday $F = Ne$.

Problem 1. Three cells containing respectively (1) copper sulfate acidified with sulfuric acid, (2) cuprous chloride in sodium chloride, and (3) cuprous cyanide with a small excess of potassium cyanide are electrolyzed for one hour with a current of one ampere with copper electrodes. What is the weight of copper dissolved at each anode and deposited at each cathode? Assume 100 percent current efficiency.

Problem 2. In a copper coulometer it is found that 1.779 g. of copper are deposited in one hour. Calculate the current.

Problem 3. In a copper-refining tank containing 30 anodes and 30 cathodes connected in parallel and each 3 feet square, the current density is 20 amperes per square foot. Calculate the current in the tank and the amount of copper deposited in 24 hours at 95 percent current efficiency.

Problem 4. Calculate the amount of aluminum deposited a day in a 10,000-ampere cell, from a fused mixture of cryolite and aluminum oxide, at a current efficiency of 80 percent.

Problem 5. Calculate the volume of chlorine produced a day in a 3750-ampere cell, by electrolyzing a solution of sodium chloride with 92 percent current efficiency. Assume the temperature of the gas to be 20° C. and the pressure 760 mm. of mercury.

Problem 6. If a current of 0.3 ampere is passed through a dilute solution of sulfuric acid for 30 minutes, what volume of hydrogen and what volume of oxygen will be produced, measured at 76 cm. and 25° C.?

CHAPTER II

THE ELECTROLYTIC DISSOCIATION THEORY AND MIGRATION OF IONS

BEFORE explaining more fully the conduction of electricity through electrolytes, it will be necessary to give an account of the *electrolytic dissociation theory*, which is of fundamental importance to electrochemistry.

Osmotic Pressure. — If a solution is placed in a tube closed at the bottom by a membrane permeable to water but not to the solute, a so-called semipermeable membrane, the solution will rise to a point B in Figure 8, drawing water in through the membrane. A semipermeable membrane may be made by precipitating cuprous ferrocyanide in the pores of a clay cup.

Osmotic pressure may be defined as the hydrostatic pressure of the column of liquid when equilibrium has been established. It may be considered to be due to the tendency of the dissolved particles to increase the volume in which they are contained, just as a gas tends to expand. It is also the cause of diffusion from a place where the concentration is high to where it is low. Osmotic pressure can
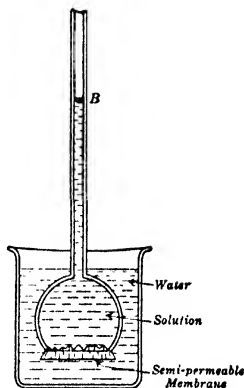
FIG. 8. — OSMOTIC PRESSURE

be observed directly only by means of an arrangement similar to the one in Figure 8, because it is overbalanced by a much greater force at the surface of a solution.

It was shown by van't Hoff in 1885 that for many dissolved substances the osmotic pressure is the same as its pressure as a gas would be if the dissolved substance were changed to a gas without decomposition and contained in the same volume that the solution occupies. It was found further that in dilute solutions the gas law equation $PV = nRT$ applies to osmotic pressure,

where P is the osmotic pressure, V the volume of the solution, n the number of mols in the solution, R the gas constant, and T the absolute temperature. The value of R may be calculated from the fact that at 273° absolute one mol of any gas has a volume of 22.42 liters at atmospheric pressure. Therefore $R = 22.42/273 = 0.0821$ liter atmospheres per degree, or 1.985 calories per degree. Since the gas law holds it is a necessary consequence that Avogadro's principle holds for these solutions; consequently at equal temperatures the number of solute molecules in a given volume is the same as the number of gas molecules in the same volume when the gas pressure is equal to the osmotic pressure.

Theory of Arrhenius. — Other properties of solutions which depend on the number of solute molecules are the raising of the boiling point, the lowering of the freezing point, and the lowering of the vapor pressure when a non-volatile substance is dissolved in a solvent. Thus, one tenth of a mol of sugar dissolved in 1000 grams of water lowers the freezing point by 0.186° and the boiling point is raised by 0.52°. The same values are found for all substances except electrolytes, which give larger values. A solution of one tenth mol of sodium chloride per liter, for example, gives nearly twice the expected freezing point lowering, nearly twice the expected rise in boiling point, and nearly twice the expected osmotic pressure. Since these deviations vary with the nature of the solute and the concentration, it may be said in general that the effect of electrolytes is i times as much as expected. This may be expressed for osmotic pressure by the equation $PV = niRT$, or for the abnormal freezing point thus:

$$\frac{\text{abnormal freezing point lowering}}{\text{normal freezing point lowering}} = i.$$

In order to account for this abnormal behavior, Arrhenius [1] proposed the theory that electrolytes are dissociated to a certain extent into positive and negative ions, thus increasing the number of solute molecules, since an ion has the same effect on these properties as a molecule. This is known as the *electrolytic dissociation theory*. This idea of electrolytic dissociation was not originated by Arrhenius, but he was the first to present the evidence that in strong electrolytes the larger part of the dissolved substance existed in the form of ions. Electrolytic differs from gaseous dissociation in that the products of electrolytic dissociation are combined with electricity and the character of the substance is

[1] Z. phys. Ch. **1**, 631 (1887).

thereby completely changed; for example, a potassium ion does not act on water.

The value of i can be computed as follows. Let x be the degree of dissociation and n the number of parts into which the electrolyte dissociates, then $i = 1 - x + nx$, from which the degree of dissociation is

$$x = \frac{i - 1}{n - 1}.$$

Ions may be either charged radicals or charged elementary substances as will be evident from the following equations of ionization:

$$NaCl \rightleftarrows Na^+ + Cl^-,$$
$$Na_2SO_4 \rightleftarrows 2 Na^+ + SO_4^{--},$$
$$K_4Fe(CN)_6 \rightleftarrows 4 K^+ + Fe(CN)_6^{----}.$$
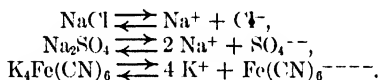
The $\rightleftarrows$ sign indicates that the reaction is reversible. It is evident that sodium chloride can dissociate in only one way, but that more complicated molecules might dissociate in more than one way. It is often possible to determine into what ions a molecule dissociates by transference measurements, as will be explained below.

Dissociating Power and Dielectric Constant. — It is found that there is a rough proportionality between the dielectric constant of solvents and their dissociating power, though this relation cannot be put in the form of an equation. Solvents with high dielectric constants, like water, dissociate dissolved substances to a high degree, while solvents with low dielectric constants dissociate dissolved substances to a less degree. This is what would be expected from the fact that the attraction of electric charges for each other is inversely proportional to the dielectric constant of the medium surrounding them.

This subject has been studied by Walden [1] who determined the conductance at infinite dilution of tetraethylammonium iodide, $N(C_2H_5)_4$, in fifty different solvents and for these particular cases found the relation to hold. It is not an infallible rule, however; [2] iodine, for example, has a higher conductance at the same dilution in acetone, whose dielectric constant is 21, than in epichlorhydrine, whose dielectric constant is 26. Conductance is not such a good

[1] Walden, Z. phys. Ch. **54**, 129 (1906); McCoy, J. Am. Ch. Soc. **30**, 1074 (1908).

[2] Shaw, J. Phys. Chem. **17**, 162 (1913).

property to compare as ionization coefficients because it involves the migration velocity which is not constant in different solvents. If the dissociation constant is taken,[1] which is a measure of the dissociation, there are still exceptions, but they are not so striking. This is shown in Table 1, which gives in parallel columns values of the equilibrium constant k and the equivalent conductance at infinite dilution of typical salts in different solvents and the dielectric constant of the solvents.[2] These data were compiled from existing measurements.

TABLE 1. DISSOCIATING POWER AND DIELECTRIC CONSTANT

SOLVENT	SOLUTE	TEMP DEG. C.	EQ. COND AT INF. DIL	$k \times 10^4$	D. C.
Water	KCl	18	128.9	about 200	80
Benzonitril	NaI	25	49	55	26
Propyl alcohol	NaI	18	20.6	45	23
Acetone	NaI	18	67	40	22
Acetophenone	NaI	25	35	44	19
Ammonia	NaI	− 33.5	301	30	19
Methylethyl ketone . .	NaI	25	139	25	18
Isobutyl alcohol . . .	NaI	25	13.7	12	18
Aceto-acetic ester . . .	NaI	18	30.7	about 15	16
Pyridine	NaI	18	61.5	11	12
Isoamyl alcohol . . .	NaI	25	9.5	4	15
Pyridine	KI	18	64	5	12
Sulphur dioxide	KI	− 10	207	7	15
	KI	10	240	4	15

THE MIGRATION OF IONS

Faraday's law indicates that the electric current is carried through solutions by the migration of ions, but says nothing about the relative or absolute velocity with which they move. This relative velocity can be determined from the concentration changes that take place at the electrodes, as was shown by Hittorf.[3] Referring to Figure 9, suppose the electrolytic cell contains 30 gram atoms of hydrogen ions and an equal number of chlorine ions, and that the cell is completely divided into three equal parts by two porous partitions placed between the electrodes. These partitions

[1] See page 42.
[2] Bray, Tr. Am. Electroch. Soc. 21, 143 (1912).
[3] Pogg. Ann., Vols. 89, 98, 103, 106 (1853–59).

do not interfere with the passage of the current but prevent mechanical mixing of the solution in the three compartments. Suppose six faradays of electricity to pass, depositing six equivalents of hydrogen on the cathode at the right and six of chlorine on the anode at the left. If (1) the current were carried entirely by positive ions, during the time that six equivalents are deposited on the electrodes six equivalents of positive ions would pass across every section of the cell and the concentration of HCl in the cathode compartment would remain unchanged, since all six positive ions liber-

Positive Current

10   10   10

Initial Condition

4   10   10

(1) 6 F passed carried entirely by + ions

5   10   9

(3) 6 F passed, 5 F carried by hydrogen, 1 F by chlorine
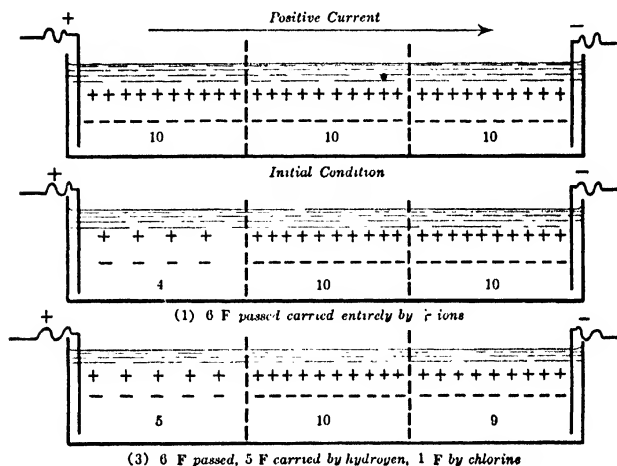
FIG 9. — MIGRATION OF IONS

ated are replaced by the six by migration and no negative ions are lost. At the anode six negative ions are lost by deposition and six positive ions have left the compartment by migration so that the concentration of the anode solution is diminished by six equivalents of HCl.

If (2) chlorine and hydrogen ions have equal velocities, they would each carry half the current. As far as the current is concerned these two cases are equivalent electrically since the motion of positive electricity in one direction is the same as the motion of an equivalent amount of negative electricity in the opposite direction. In this case the cathode would lose six equivalents

of hydrogen by deposition but would gain three by migration and would therefore have a net loss of three equivalents. There would also be a loss of three equivalents of chlorine by migration so that the loss in hydrochloric acid in the cathode compartment would be three equivalents. At the anode the conditions would be similar with a loss of three equivalents of hydrochloric acid.

Finally (3), if hydrogen ions move with five times the velocity of chlorine ions, as is actually the case, then five equivalents of hydrogen cross every section of the cell toward the right while one of chlorine crosses to the left. The resulting concentrations are then those represented in (3) Figure 9. In the cathode compartment six equivalents of hydrogen are deposited but five migrate in, with a net loss of one equivalent. One equivalent of chlorine is lost by migration and the cathode compartment therefore loses one equivalent of hydrochloric acid. Similar reasoning will show that the anode loses five equivalents. From this it is clear that the following relation holds:

$$\frac{\text{Velocity of cation}}{\text{Velocity of anion}} = \frac{U_c}{U_a} = \frac{\text{Loss in equivalents at anode}}{\text{Loss in equivalents at cathode}}$$

$$= \frac{\text{Equivalents of cation transferred to cathode}}{\text{Equivalents of anion transferred to anode}}.$$

From this it follows by proportion that

$$\frac{U_c}{U_c + U_a} = \frac{\text{Equivalents of cation transferred to cathode}}{\text{Total equivalents of ions transferred in both directions}}.$$

This fraction is called the **transference number** or **transport ratio** of the cation, n_c, and $U_a/U_a + U_c = n_a$ is the transference number of the anion. Evidently $n_c + n_a = 1$; that is, the sum of the equivalents of positive and negative ions that cross any section of the electrolyte when one faraday passes equals unity. The same considerations apply to polyvalent ions.

In making transference measurements it is necessary to keep the contents of the anode and cathode compartments completely separate, and many different cells have been devised for this purpose. Figure 10 shows a transference cell suitable for laboratory experiments where the concentration change is to be determined only at one electrode.[1] For determining the trans-

[1] Ostwald-Luther, *Hand- und Hülfsbuch*, p. 504 (1920).

ference number of silver in silver nitrate the right-hand branch is partly filled with concentrated copper nitrate solution, the rest of the cell with a twentieth-normal solution of silver nitrate. A current of 10 milliamperes is passed for about two hours through
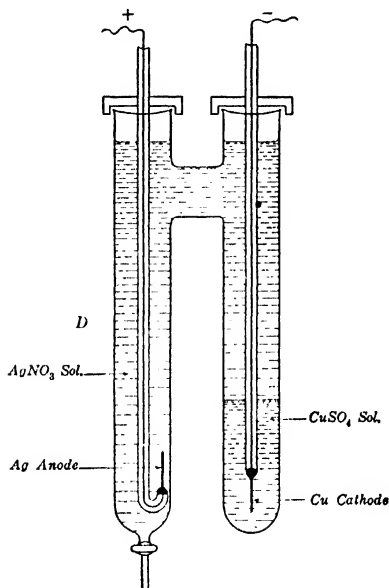
FIG. 10. — CELL FOR DETERMINING TRANSFERENCE
NUMBERS

the cell with a silver coulometer connected in series. The following data illustrate the calculation.

Before experiment, content of 1 g. water . . .   0.00739 g. AgNO₃
Weight of anode portion after experi-
  ment leaving level at D . . . .   23.38 g.
Anode portion contained . . . .   0.2361 g. AgNO₃
Weight of water in anode portion . . . . .   23.14 g.
Content of this weight of water before
  experiment . . . .   0.1710 g. AgNO₃
Gain in anode portion . . . .   0.0651 g. AgNO₃
                                      or 0.000383 equivalent
Deposited in coulometer . . . .   0.000723 equivalent Ag

The same amount must have dissolved at the anode, therefore the amount that migrated from the anode compartment is $0.000723 - 0.000383 = 0.000340$ equivalent. The transference number of silver is therefore $0.000340/0.000723 = 0.470$. The middle portion is also always drawn off and analyzed to be sure its concentration remained unchanged.

Table 2 gives the transference numbers of some of the more important electrolytes.[1]

TABLE 2. CATION TRANSFERENCE NUMBERS AT DIFFERENT TEMPERATURES
Noyes and Falk, J. Am. Chem. Soc. **33**, 1454 (1911)

SUBSTANCE	TEMP	CONCENTRATION, IN NORMALITY					
		.005	0.01	0.05	0.1	0.5	1.0
NaCl	0	0.387	0.387	0.386	0.385		
	18	0.396	0.396	0.395	0.393	0.382	0.369
	30	0.404	0.404	0.404	0.403		
KCl	0	0.493	0.493	0.493	0.492		
	18	0.496	0.496	0.495	0.495		
	30	0.498	0.498	0.498	0.497		
LiCl	18		0.332	0.320	0.313		
NH_4Cl[2]	0		0.489				
	18		0.492	0.492			
	30		0 495				
NaBr	18	0.395	0.395				
KBr	18		0.495				
$AgNO_3$	18		0.471	0.471	0.471		
	30	0.481	0.481	0.481	0.481	0.481	
HCl	0	0.847	0.846	0.839	0.834		
	18	0.832	0.833	0.834	0.835	0.840	0.844
	76				0.781		
HNO_3	20	0.839	0.840	0.844			
$BaCl_2$	0	0.439	0.437				
	25			0.438	0.427		
	50		0.475				
$Ba(NO_3)_2$	25			0.456	0.456		
$MgSO_4$	18	0.388	0.385	0.373			
K_2SO_4	18		0.494	0.490			
	25			0.496	0.494		
$CuSO_4$				0.375	0.373	0.327	
H_2SO_4	20			0.822	0.822	0.816	0.812
KOH[1]	18				0.265	0.262	0.260
NaOH[1]	18			0.19	0.18	0.18	0.175

[1] Noyes and Falk, J. Am. Chem. Soc. **33**, 1454 (1911).
[2] From Kohlrausch and Holborn, *Leitvermögen der Elecktrolyte* (1916).

The Change of Transference Numbers with Temperature and Concentration. — Table 2 shows that transference numbers are functions of the concentration, and that the effect of concentration is more marked at high concentrations than at low. In dilute solutions limiting values are approached. In general, at higher concentrations the transference number of the more slowly moving ion decreases.[1] This change with the concentration is probably due to a change in the viscosity of the solution and to a change in the hydration of the ions. It is also possible that complex ions may form at higher concentrations, such as $BaCl_4^{--}$ or $Mg(SO_4)_2^{--}$.

Transference numbers approach 0.5 with increasing temperature. This is due to the fact that at higher temperatures the conductances of the ions become more nearly equal, probably due to the hydration of the more rapidly moving ions increasing and approaching that of the more slowly moving ions.[2]

The conductance of the more slowly moving ion changes almost in exact proportion to the fluidity change of the solvent, which would indicate that the approaching equality of the two conductances is not due to the loss of water by the slowly moving ion. That transference numbers approach the value 0.5 would also be partly due to the fact that if the numerator and denominator of a fraction are each increased by approximately equal amounts, the value of the fraction becomes more nearly equal to 0.5. Thus if a and b are the mobilities of two ions at 25° and $a + x$ and $b + y$ the corresponding values at 50°, then if x and y were equal,

$$\frac{a + x}{a + x + b + y} \quad \text{and} \quad \frac{b + y}{a + x + b + y}$$

would both be nearer 0.5 than

$$\frac{a}{a + b} \quad \text{and} \quad \frac{b}{a + b}.$$

Moving Boundary Method of Determining Transference Numbers. — It is evident from the equation $U_c / U_c + U_a = n_c$ that if the velocities of the ions could be measured directly, this would give another method of determining transference numbers. This has been done[3] by means of an apparatus represented in

[1] Kraus, *The Properties of Electrically Conducting Systems*, p. 25 (1922).
[2] Kraus, *l.c.*, pp. 202 and 124.
[3] Denison and Steele, Z. phys. Ch. **57**, 110 (1907); Denison, Tr. Faraday Soc. **5**, 165 (1909).

Figure 11. A solution of the salt to be investigated, for example sodium chloride, is placed in the tube between the solutions of two other salts, each with an ion common to sodium chloride, such as lithium chloride and sodium acetate. The current is passed for a given time in the direction shown during which the boundary a moves to a' and b to b'. In order to keep the boundaries sharp the lithium ion must have a smaller velocity than the sodium and the acetate must have a smaller velocity than the chloride. These conditions are fulfilled for these salts. bb' then represents the distance moved by the sodium ion while the chloride ion moves the distance aa'. These distances must be corrected for the volume changes taking place at the electrodes.[1] The transference number of sodium is then $\dfrac{bb'}{aa' + bb'}$. The boundaries are visible on account of the difference in the indices of refraction of the solutions. The results obtained by this method agree with those by the Hittorf method, but have a higher degree of reproducibility, and can give correct results if the conditions are properly chosen.

True Transference Numbers. — Neither of the methods for determining transference numbers just described gives true transference numbers, except in dilute solutions, on account of the hydration of ions, and consequent motion of water with the ions. If the cation of a salt has more molecules of water attached to it than the anion, then after an electrolysis there will be more water in the cathode compartment than if the two ions were equally hydrated. Suppose the net number of mols of solvent transferred to the cathode compartment per faraday is ΔN and that

FIG. 11. — TRANSFERENCE BY MOVING BOUNDARY METHOD

Li Cl

b

b'

Na Cl

a'

a

CH₃COONa

[1] Lewis, J. Am. Ch. Soc. **32**, 862 (1910).

in the solution there are N_s equivalents of solute to N_w equivalents of water, then the relation between the true cation transference number n_c^{tr} and the ordinary Hittorf transference number n_c^H is,

$$n_c^{tr} = n_c^H + \Delta N \frac{N_s}{N_w} \; ; \text{ for the anion, } n_a^{tr} = n_a^H - \Delta N \frac{N_s}{N_w}$$

since in the analysis of the cathode compartment too little salt would be found by the amount $\Delta N(N_s/N_w)$ per faraday. True transference numbers have been obtained by using a stationary reference substance such as raffinose.[1] These experiments consist in determining the concentration of the raffinose in the anode or the cathode compartment before and after the experiment as well as the change in the quantity of salt in the•compartment in question. From the change in the concentration of the raffinose or other indicator as measured by a polariscope the quantity of water transferred can be computed. Of course blank tests have to show that the indicator does not migrate under the influence of the potential gradient. Table 3 gives some results of such measurements.

TABLE 3. HYDRATION OF IONS IN 1.3 NORMAL SOLUTIONS

SALT	MOLS OF WATER CARRIED FROM ANODE TO CATHODE PER FARADAY	TRUE TRANSFERENCE NUMBER OF CATION	TRANSFERENCE NUMBER OF CATION INF DILUTION	HITTORF TRANSFERENCE NUMBER OF CATION	MOLS WATER ON CATION WHEN ANION IS ASSUMED TO HAVE		
					0	4	10
HCl	0.24 ± 0.01	0.844	0.833	0.82	0.28	1.0	2.1
CsCl	0.33 ± 0.06	0.491	0.491	0.485	0.67	4.7	11.0
KCl	0.60 ± 0.08	0.495	0.495	0.482	1.3	5.4	11.5
NaCl	0.76 ± 0.08	0.383	0.396	0.366	2.0	8.4	18.0
LiCl	1.5 ± 0.1	0.304	0 330	0 278	4.7	14.0	28.0

From this table it is seen that 0.24 mol of water is transferred to the cathode compartment with 0.84 mol of hydrogen; therefore, if the chloride has no water of hydration, the least amount of water that can be attached to one mol of hydrogen is $0.24/0.84 = 0.28$ mol. Suppose next that the chloride ion has four mols attached to it; then the hydrogen ion must still carry enough more water molecules to make the net result the same. That is, if x is the number of mols of water attached to the hydrogen ion, then

[1] Washburn, J. Am. Ch. Soc. 31, 322 (1909); Washburn and Millard, ibid. 37, 694 (1915).

$0.884\ x - 0.156 \times 4 = 0.24$, whence $x = 1$. The other values in the last two columns are similarly calculated. If there were any method of finding the hydration of a single ion, the others could be determined, but no such method has yet been found.

Solutions with More Than One Electrolyte.—In case the solution contains more than one electrolyte, all of the cations migrate to the cathode and all of the anions to the anode, just as when only one salt is present. The proportion of the current carried by each salt will depend on the concentration and the dissociation of the salt and the velocity of migration of its ions. This was shown by Hittorf by electrolyzing a solution containing both potassium iodide and chloride. Since the transference number of these salts is the same, their relative concentrations should remain unchanged throughout the cell, except in the anode compartment, where a change would occur on account of the fact that only iodine is set free. This was confirmed by experiment. This calls attention to the important fact that *the ions that are liberated at the electrodes are not necessarily the ones that carry the current through the solution.* As will be explained later, those ions are deposited whose deposition requires the least energy, and this has nothing to do with transference or the conductance of the solution.

Constitution of Electrolytes from Transference Numbers. — The determination of transference numbers shows, in some cases, the kinds of ions into which an electrolyte dissociates. For example, a transference experiment in a solution of $KAg(CN)_2$ shows that silver migrates to the anode, therefore silver must be in the anion $Ag(CN)_2^-$. Similarly, the iron in $K_4Fe(CN)_6$ migrates to the anode, showing that it is contained in the complex anion $Fe(CN)_6^{----}$, and platinum in Na_2PtCl_6 is in the anion $PtCl_6^{--}$.

Acids dissociate into hydrogen and the acid radical, but acids with more than one hydrogen atom may dissociate in different ways, as sulfuric acid, which dissociates as follows:

(1) $H_2SO_4 = H^+ + HSO_4^-$ and (2) $H_2SO_4 = 2\ H^+ + SO_4^{--}$.
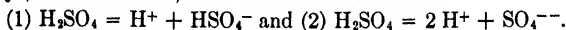
In concentrated sulfuric acid solutions ionization takes place principally according to (1), and (2) takes place to a greater extent the greater the dilution. In a 0.1 normal solution the acid is ionized to 67 percent according to (1) and 27 percent according to (2).[1]

[1] Harkins, J. Am. Ch. Soc. **33**, 1868 (1911); Noyes and Stuart, *ibid.* **32**, 1133 (1910).

Bases dissociate into metal ions and hydroxyl ions. Salts dissociate into positive ions other than hydrogen and negative ions other than hydroxyl ions. Acid salts give at least one hydrogen ion in addition to some other positive ion, for example :

$$NaHSO_4 = Na^+ + H^+ + SO_4^{--},$$
$$K_2HPO_4 = 2 K^+ + H^+ + PO_4^{---}.$$
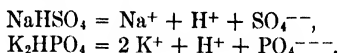
Basic salts give at least one hydroxyl ion in addition to another negative ion, thus :

$$Fe(OH)_2Cl = Fe^{+++} + 2 OH^- + Cl^-.$$
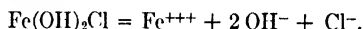
An amphoteric electrolyte is one which gives both hydrogen and hydroxyl ions :

$Pb(OH)_2 = 2 H^+ + PbO_2^{--}$ in the presence of hydroxyl ions;
$Pb(OH)_2 = Pb^{++} + 2 OH^{--}$ in the presence of hydrogen ions;
$Zn(OH)_2 = Zn^{++} + 2 OH^{--}$ in the presence of hydrogen ions;
$Zn(OH)_2 = H^+ + HZnO^-$ in the presence of hydroxyl ions.
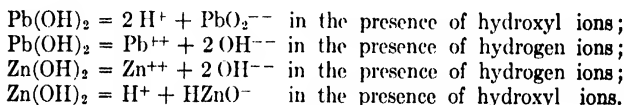
Transference Numbers in Non-aqueous Solutions. — Transference numbers have been determined in non-aqueous solutions, for example, in liquid ammonia, by the moving-boundary method.[1] Ions in this solvent move with greater velocity than in water, on account of the smaller viscosity of liquid ammonia. Transference numbers for a given salt vary with the solvent, showing that the relative migration velocity changes with the solvent.

A few transference numbers determinations have been made in fused electrolytes, with interesting results. Thus Lorenz and Fausti[2] found that in a mixture of lead and potassium chlorides, lead migrates to the anode and is therefore combined with chlorine to form a complex anion. By electrolyzing glass with a sodium amalgam anode and a mercury cathode, it was found that the amount of sodium which enters the mercury cathode from the glass electrolyte is equivalent to the quantity of electricity passed and that the glass had not changed its weight or transparency. From this it must be concluded that in glass only the sodium ion migrates while the silicate ion remains stationary or very nearly so.[3] Another example where the cation migrates and the anion does not is solid silver iodide.[4]

[1] Franklin and Cady, J. Am. Ch. Soc. **26**, 499 (1904).
[2] See Lorenz, *Elektrolyse geschmolzener Salze*, **2**, 159 (1905).
[3] Warburg, Ann. d. Phys. **21**, 622 (1884).
[4] Lorenz, *Elektrolyse geschmolzener Salze*, **2**, 152 (1905).

Sodium can be deposited on the inside of electric-light bulbs by immersing the bulb in melted sodium nitrate at about 450° C., heating the filament, and applying 200 volts between the nitrate and the filament. This is due to the migration of sodium through the glass wall of the bulb. This can be used to remove the film of water vapor on the inside of bulbs which cannot be removed by heat.[1]

Problem 1. An electrolytic cell is divided by two diaphragms into three compartments of 500 cc., each filled with a normal solution of sodium hydrate. A current of 2 amperes is passed for 14 hours and the diaphragms are supposed to have no effect except to prevent mechanical mixing. What is the final amount of sodium hydrate in the cathode compartment? The transference number of the sodium ion is 0.175.

Problem 2. The cell in problem 1 is filled with a half-normal solution of copper sulfate and is electrolyzed for 3 hours with 4 amperes, using copper electrodes. Calculate the concentrations of copper sulfate in the two compartments after the run. The transference number of copper in copper sulfate is 0.327.

Problem 3. If, in copper-refining tanks, the solution were not stirred, how would the concentration alter in different parts of the tank?

[1] Pirani and Lax, Z. tech. Phys. **3**, 232 (1922).

CHAPTER III

ELECTRICAL CONDUCTANCE

Definitions. — Electrical conductance is the reciprocal of resistance and is expressed in *reciprocal ohms*, also called *mhos*. In giving numerical values to the conductance of any substance or solution a definite geometrical form must be selected for comparison, such as a centimeter cube or inch cube. The conductance between two opposite faces of the cube is called the *specific conductance* or *conductivity*, and the size of the cube must be given. The centimeter cube is that usually chosen. Specific conductance referred to this unit is usually designated by κ. From this the conductance of any right prism or cylinder of length l and cross-section s may be calculated by the formula,

$$\text{Conductance} = \frac{1}{R} = \frac{\kappa s}{l} \text{ mhos.}$$

From a theoretical point of view a far more important basis of comparison for electrolytes is the conductance of one equivalent weight, either in solution or in the fused state, when placed between two parallel conducting plates one centimeter apart. In Figure 12 the two vertical faces which are one centimeter apart are supposed to be metallic, while the bottom and ends of the vessel are glass or some other non-conductor. If a solution containing one equivalent weight of an electrolyte is placed in this vessel and the conductance

FIG. 12. — EQUIVALENT CONDUCTANCE

measured, the value obtained is the equivalent conductance, represented by Λ with a subscript indicating the concentration or the dilution. The relative length and depth of this vessel have no
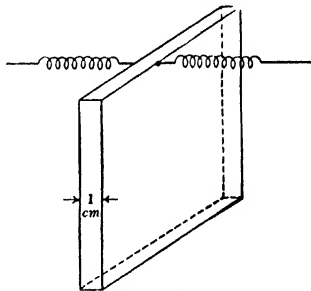
effect on the result; it is only required that the volume be sufficien·
to contain an equivalent weight of the electrolyte.

Conductance Measurement. — Actual measurements are of
course not made in a cell of this kind. The specific conductance
is measured in a cell of convenient shape and the equivalent con-
ductance is computed by the formula:

$$\Lambda = 1000\,\kappa \cdot v = \frac{1000\,\kappa}{c}.$$

κ is the specific conductance, v is the dilution or number of liters
containing one equivalent, and c is the number of equivalents in
one liter. Various forms of cells have been devised for con-
ductivity, some of which are shown in Figure 13. Figure

13 (a) represents
the cell most
commonly used
for instruction
purposes. *A A*
are platinum elec-
trodes covered
with electrically
deposited plati-
num black to in-
crease the sur-
face. They are
held by set-
screws in a vul-
canite cover.

(a)   (b)   *For Solutions of High Conductivity*
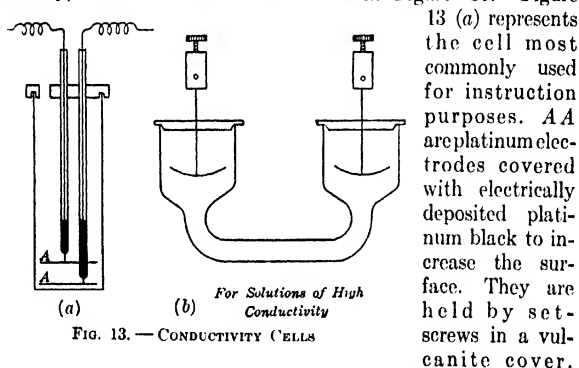
FIG. 13. — CONDUCTIVITY CELLS

The constant of the cell is determined by measuring the conduc-
tance of some solution whose specific conductance is known. In
making measurements the depth of the solution above the top
electrode does not affect the result, as the electrodes fit the cell
closely. If the conductance of the cell containing the standard
substance of specific conductance κ is m mhos, then the cell con-
stant $k = \kappa/m$. Multiplying the conductance of the cell con-
taining any electrolyte by k will give its specific conductance.
Potassium chloride solutions are generally used for determining
cell constants. Values for different temperatures and concentra-
tions are given in Table 4.[1]

[1] Kohlrausch, Holborn, and Diesselhorst, Ann. d. Phys. **64**, 417 (1898).
The normal solution is made by dissolving 76.727 g. KCl (weighed in air) in

TABLE 4. SPECIFIC CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS

NORMALITY	κ AT 18° C.	κ AT 25° C.
1.0	0.09822	0.11180
0.1	0.01119	0.01288
0.02	0.002397	0.002765
0.01	0.001225	0.001413

On account of polarization, a direct current is not generally used for measuring the conductance of electrolytes, though it can be done by taking certain precautions.[1] Usually the Wheatstone bridge is used with an alternating current such as is furnished by a small induction coil or better, by a generator with a frequency of 1000 cycles a second. A telephone is used in place of a galvanometer; if great sensitiveness is required, the telephone should be tuned to the frequency of the generator.[2] The connections are shown in Figure 14. AB represents a fine platinum-iridium or manganin wire one meter long stretched on a meter scale divided in millimeters. C is the generator, D a sliding contact, R an adjustable non-inductive resistance box, E the telephone, and X the cell. In making a
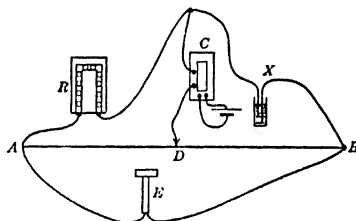
FIG. 14. — APPARATUS FOR DETERMINING ELEC-
TROLYTIC CONDUCTIVITY

measurement the resistance in R is changed until the minimum sound in the telephone occurs when D is somewhere near the middle of the bridge. When the balance is found, the following proportion holds, assuming the resistance of the wire AB is proportional to its length:

1 l. of water at 18° [Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, p. 76 (1916)]. The other solutions can be made from this by dilution, with sufficient accuracy for ordinary work. For the procedure for the most exact work, see Kraus and Parker, J. Am. Ch. Soc. **44**, 2422 (1922).

[1] Marie and Noyes, J. Am. Ch. Soc. **43**, 1905 (1921); Eastman, J. Am. Ch. Soc. **42**, 1648 (1920).

[2] Washburn and Bell, J. Am. Ch. Soc. **35**, 177 (1913).

$$\text{res. } R : AD \text{ mm. } = \text{res. } X : DB \text{ mm.}$$

$$\text{or conductance of } X = \frac{1}{\text{res. } R} \cdot \frac{a}{1000 - a}.$$

The accuracy of the measurements may be increased by placing extension coils at each end of the slide-wire.

Problem 1. Calculate the resistance of the electrolyte of a copper-refining tank of the multiple system, containing 30 anodes and 30 cathodes 3 feet square whose surfaces are 1.25 inches apart. The specific resistance of the electrolyte containing sulfuric acid, copper sulfate, and impurities is 0.8 ohm per cubic inch at 53° C., the temperature of operation. *Ans.* 0.000027 ohm. The total tank resistance would be about twice this value.

Gram Equivalents per Liter
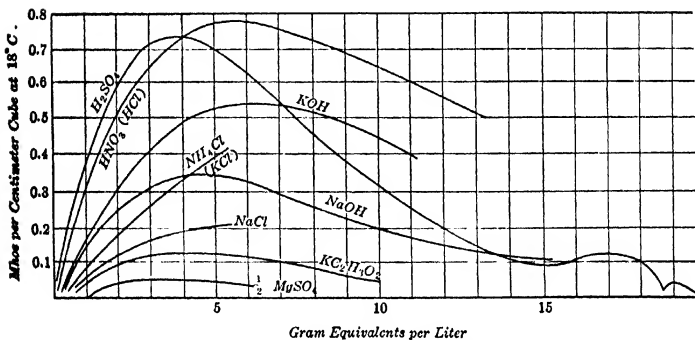
FIG. 15. — SPECIFIC CONDUCTANCE

Concentration and Conductance. — The specific conductance, of any dissolved substance depends on (1) the concentration of the ions, (2) their velocity of migration, and (3) their charge. The concentration of the ions depends on the concentration of the electrolyte and its ionization, as will be shown below. Starting with a dilute solution, the specific conductance always increases at first with increase of concentration of the electrolyte on account of the larger number of ions, but the decreased ionization and the increased friction to the motion of the ions sometimes causes the conductivity to pass through a maximum, as in Figure 15. In other cases saturation is reached before this occurs.

The equivalent conductance, on the other hand, increases continuously with the dilution until a limiting value is reached.

According to the dissociation theory this is due to the increasing ionization with the dilution, until at high dilutions all of the electrolyte is ionized. These limiting values of the equivalent conductance at infinite dilution are found by extrapolation. Various methods of making this extrapolation have been proposed.[1]

TABLE 5. EQUIVALENT CONDUCTANCE AND CONCENTRATION
Noyes and Falk, J. Am. Ch. Soc. **34**, 454 (1921)

ELECTROLYTE	CONCENTRATION IN EQUIVALENTS PER LITER									
	0		0.001		0.01		0.1		1.0	
	18°	25°	18°	25°	18°	25°	18°	25°	18°	25°
NaCl	108.9	127.0	106.4	124.1	101.97	118.7	91.96	106.8	74.31	
KCl	130.0	150.6	127.27	- - -	122.37	141.4	111.97	129.0	98.22	
LiCl	98.8		96.34		91.97		82.28		63.27	
TlCl	131.4		128.23		120.21		- - - - -		-----	
NH₄Cl	130.2		- - - -		122.5		- - - -		-----	
KBr	132.2		129 28		124.31		114.14		-----	
KI	131.1		128.25		123.44		113.98		103.60	
KF	111.2		108.80		104.19		93.94		75.95	
NaNO₃	105.2		102.75		98.07		87.16		65.81	
AgNO₃	115.8		113.14		107.80		94.33		67.6	
KClO₃	119.6		116.92		111.64		99.19		- - - -	
HCl	380.0	426.0	375.9	420 4	369.3		351.4			
HNO₃	376.5	420.0	372.9	-----	365.0	406.0	346.4	385.0	310.0	
CaCl₂	117.4		111.96		103.37		88.19		67.54	
ZnSO₄	115.5		98.6		72.9		45.4		26.2	
CuSO₄	114.4		98.56		71.71		43.85		25.77	
K₄Fe(CN)₆	159.5	185.0	-----		113.4		84.9		-----	
NH₄OH	(239)		28		9 60		3.30		0.89	

Independent Migration of Ions. — It was shown by Kohlrausch[2] that the limiting value of the equivalent conductance of a binary electrolyte is the sum of two conductances, one belonging to the cation, the other to the anion. This is known as *Kohlrausch's Law of the Independent Migration of Ions*, and is expressed by the equation $\Lambda_0 = \Lambda_0^+ + \Lambda_0^-$. If the Λ_0 values for all the ions are known, the equivalent conductance at infinite dilution for any

[1] Randall, J. Am. Ch. Soc. **38**, 788 (1916); Washburn, J. Am. Ch. Soc. **40**, 122 (1918); **42**, 1077 (1920); Bates, J. Am. Ch. Soc. **35**, 526 (1913); Kraus and Bray, J. Am. Ch. Soc. **35**, 1320 (1913).
[2] Wied. Ann. **6**, 1 (1878) and 145 (1879); **26**, 213 (1885).

electrolyte dissociating into two kinds of ions can be calculated by adding the values for the ions. Thus Λ_0 for hydrogen at 18° C. is 314, for chlorine 65.5; therefore Λ_0 for hydrochloric acid is 379.5 reciprocal ohms.

Table 6 gives the equivalent conductances for the most important ions.[1]

TABLE 6. EQUIVALENT CONDUCTANCES OF IONS AT 18° AND 25° C.

	18°	25°		18°	25°		18°	25°
Cs+	68.0		Ba++	55.4	65.2	Cl-	65.5	75.8
Rb+	67.5		Ca++	51.9	60.0	NO3-	61.8	70.6
Tl+	65.9	76.0	Sr++	51.9		SCN-	56.7	
NH4+	64.7		Zn++	47.0		ClO3-	55.1	
K+	64.5	74.8	Cd++	46.4		BrO3-	47.6	54.8
Ag+	54.0	63.4	Mg++	45.9	55.0	F-	46.7	
Na+	43.4	51.2	Cu++	45.9		IO3-	34.0	
Li+	33.3		La+	61.0	72	SO4--	68.5	80.0
H+	314.5	350	Br+	67.7		C2O4--	63.0	72.7
Pb++	60.8	71.0	I+	66.6	76.5	Fe(CN)6----	95.0	110.5
			OH-	172	192			

An attempt has been made to explain the abnormally high conductance of the hydrogen and hydroxyl ions in water to an interchange between the solvent molecules and the ions so that the mean path of an ion is reduced by the diameter of the solvent molecule for each interchange. This Grotthuss kind of conduction is supposed added on to the ionic migration [Danneel, Z. Electroch. 11, 249 (1905); Hantzsch and Caldwell, Z. phys. Ch. 58, 575 (1907); Lorenz, Z. phys. Ch. 82, 615 (1913)]. Kraus points out, however, that it is not generally true ions common to the solvent have abnormally high conductances, and that the true explanation is probably that the hydrogen and hydroxyl ions have less water of hydration [*Properties of Conducting Systems*, p. 209 (1922)].

Absolute Velocity of Ions. — The absolute velocity of ions in centimeters per second can be calculated from their equivalent conductance and the value of the faraday. The relation between these may be deduced as follows.

Suppose that between two electrodes one centimeter apart there is one equivalent of a uni-univalent salt at infinite dilution, and that one volt is impressed. Then the current which passes is $I = 1/R = \Lambda_0$. Suppose the positive ion moves at the rate of

[1] Noyes and Falk, J. Am. Ch. Soc. 34, 479 (1921); the OH- ion from Johnson, J. Am. Ch. Soc. 31, 1015 (1909).

U_0^+ cm. per sec. when the potential difference is one volt, and the negative ion at the rate of U_0^- cm. per sec. These velocities are directly proportional to the potential gradient, since the velocity of a particle moving in a medium of great frictional resistance is proportional to the force acting on the particle and the force on a charged particle in an electric field is $f = q\mathbf{E}/l$, where q is the charge on the particle and $\mathbf{E}/l$ is the potential gradient. The quantity of electricity carried across every cross-section in a second by the positive ions equals the product of the velocity of the ions and the charge carried, or $\mathbf{F}U_0^+$ and for the negative ions, $\mathbf{F}U_0^-$. But by definition the sum of the quantities of positive and negative electricity passing any cross-section in a second is the current, therefore

$$I = \mathbf{F}(U_0^+ + U_0^-) = \Lambda_0 \text{ and } U_0^+ + U_0^- = \Lambda_0/\mathbf{F}.$$

Therefore the sum of the velocities of the ions in centimeters per second can be calculated by dividing the conductance at infinite dilution by the value of the faraday. Thus the sum of the velocities of potassium and chlorine ions at 18° when the potential gradient is one volt per centimeter is $130/96500 = 0.00134$ cm./sec. The velocities of the single ions may be found by means of the transference numbers, for

$$n_a = U_0^+/U_0^+ + U_0^- = \mathbf{F}U_0^+/\mathbf{F}(U_0^+ + U_0^-) = \mathbf{F}U_0^+/\Lambda_0$$

and from this

$$U_0^- = n_a\Lambda_0/\mathbf{F} \text{ and } U_0^+ = n_c\Lambda_0/\mathbf{F}. \qquad (1)$$

One method of calculating the conductance of single ions comes from this equation by writing it in the form

$$n_c\Lambda_0 = \mathbf{F}U_0^+ = \Lambda_0^+ ; \qquad (2)$$

that is, the equivalent conductance of the salt is multiplied by the transference number to get the conductance of the corresponding ion. Having found the conductances of the ions of one salt by transference measurements in the most dilute solution possible, all others can be found by subtraction, for, if the single conductances of the ions in potassium chloride are known, the conductances of the ions of all metals having soluble chlorides may be obtained by subtracting the conductance of the chloride ion from the conductances of these salts at infinite dilution. The other method is to use the transference number of each salt in combination with its conductance at infinite dilution.

Problem 2. From the transference number for NaCl (Table 2) and the conductance at infinite dilution (Table 5) calculate the conductance of the sodium and chloride ions. From this and the conductance at infinite dilution of potassium chloride, calculate the conductance of the potassium ion. Also calculate the conductance of the potassium ion from the transference number of potassium chloride and its conductance at infinite dilution.

Dissociation or Ionization. — In the above derivations the electrolyte was assumed to be completely dissociated. If it were only dissociated to γ percent, then the conductance would be given by the equation

$$\Lambda = \gamma \mathbf{F}(U^+ + U^-). \tag{3}$$

Dividing this by $\Lambda_0 = \mathbf{F}(U_0^+ + U_0^-)$, we have

$$\gamma = \Lambda/\Lambda_0, \tag{4}$$

assuming that $U^+ + U^- = U_0^+ + U_0^-$. Therefore the ionization of a binary electrolyte is given by the ratio of the conductance at the concentration in question to the conductance at infinite dilution *if the velocity of migration remains constant.* This does not apply to such electrolytes as sulfuric acid, which can dissociate in more than one way.

In the case of strong electrolytes this assumption of the constancy of mobility is, however, not justified, as is shown by the change in transference number with the concentration, and except in high dilution Λ/Λ_0 cannot be an accurate measure of dissociation. It has been proposed that strong electrolytes are 100 percent ionized at all concentrations and that the decrease in equivalent conductance with increasing concentration is wholly due to the decrease in the mobility of the ions.[1]

In place of using the expression $\dfrac{\Lambda}{\Lambda_0}$ for the degree of dissociation, this has frequently been multiplied by the ratio of the viscosity of the solution to that of the pure solvent, η/η_0, giving the equation

$$\gamma = \frac{\Lambda\eta}{\Lambda_0\eta_0}. \tag{5}$$

This is for the purpose of correcting for the different frictional resistances to the motion of ions in solutions of the two concentrations, and is based on the assumption that the equivalent

[1] Noyes and MacInnes, J. Am. Ch. Soc. **42**, 239 (1920); Milner, Phil. Mag. **36**, 214 and 352 (1918); Bjerrum, Z. Elektroch. **24**, 321 (1918); Sutherland, Phil. Mag. **14**, 1 (1907); Ghosh, J. Ch. Soc. **113**, 449, 627, 790 (1918).

conductance of an ion is inversely proportional to the viscosity of the medium through which it moves; that is,

$$\frac{U^+ + U^-}{U_0^+ + U_0^-} = \frac{\eta_0}{\eta}.$$

Substituting this in

$$\frac{\Lambda}{\Lambda_0} = \gamma \, \frac{U^+ + U^-}{U_0^+ + U_0^-},$$

we have equation (5). This correction, however, is now generally considered of doubtful validity.

It is possible that salts in the crystal state are completely ionized, or more strictly, polarized; that is, the atoms in the crystal are charged; Langmuir is led to this conclusion by his theory of the structure of the atom, and this is supported by X-ray crystal analysis which gives no evidence of molecules in crystals.[1]

There is even doubt as to just what is meant by dissociation. Tolman says:[2]

" If we could see into a salt solution with a super-microscope, it would be difficult to tell whether a given molecule were dissociated or not, as the molecules would be in all possible stages between complete dissociation and no dissociation. It is possible that, for instance, an ion but slightly removed from its parent molecule might be able to affect the conductivity whereas it might not be able to affect the electromotive force of an electrode, and thus determinations of ionization by conductivity would be expected to differ from those determined by electromotive force or freezing point determinations."

Degree of Ionization. — Table 7 gives the degrees of ionization from conductance ratios for different types of salts at different concentrations. Evidently salts of the same type have nearly the same dissociation at the same concentration, but different types have quite different values. The general statement can be made that all salts are highly dissociated in dilute solutions, with the exception of mercury and cadmium halides, which for some unknown reason are less dissociated.

[1] J. Am. Ch. Soc. **42**, 274 (1920). For a discussion of the classification of bodies as polar or non-polar, see Lewis, J. Am. Ch. Soc. **35**, 1448 (1913).

[2] Lewis, Physical Chemistry, Vol. 2, p. 231. See also Lewis and Randall, J. Am. Ch. Soc. **43**, 1112 (1921).

TABLE 7. DEGREES OF DISSOCIATION $\left(100\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)$ FOR DIFFERENT TYPES OF SALTS

Noyes and Falk, J. Am. Ch. Soc. **34**, 474 (1912)

TYPE	SALT	NORMALITY			
		0 001	0.01	0 1	1.0
Uni-univalent	KCl	97.9	94.1	86.0	74.2
	NaNO$_3$	97.7	93.5	82.4	61.3
Uni-bivalent	BaCl$_2$	95.6	88.3	75.9	64.2
	K$_2$SO$_4$	95.4	87.2	72.2	59.2
Bi-bivalent . . . . . .•	CuSO$_2$	86.2	62.9	39.6	30.9
	ZnSO$_4$	85.4	63.3	40.5	30.9

No theoretical significance is to be attached to the values of ionization for salts of the uni-bivalent or of higher types, because of the possible formation of intermediate ions.

With acids and bases all degrees of dissociation are found, as shown in Table 8.[1]

TABLE 8. DISSOCIATION OF ACIDS AND BASES, 18° C.

ELECTROLYTE	NORMALITY			
	0 001	0 01	0 1	1 0
HCl	99.0	97.2	92.2	79.1
HNO$_3$	99.5	97.7	92.9	82.3
CH$_3$COOH	12	4.1	1.3	0.38
NaOH	95.6	91.9	84.1	73.6
NH$_4$OH	11.8	4.0	1.4	0.37

In order to indicate that a substance is not all in the ionic state, but that some is undissociated, the term *ion-constituent* is used. Thus the equivalent conductance of an ion Λ_0 is the conductance of one equivalent weight in the ionic state; the equivalent conductance of an ion-constituent is the conductance Λ_c of that part of an equivalent which is ionized.   If γ is the dissociation,

$$\Lambda_c = \gamma\Lambda_0$$

[1] This table calculated from data on pages 168, 169, 214, and 216 of 2 ed. of Kohlrausch and Holborn's *Das Leitvermögen der Elektrolyte.*

Conductance and Temperature. — The conductances of metallic conductors in general decrease with rise in temperature. Exceptions to this rule are carbon, boron, and silicon carbide. For electrolytic conduction the reverse is true. In aqueous solutions,
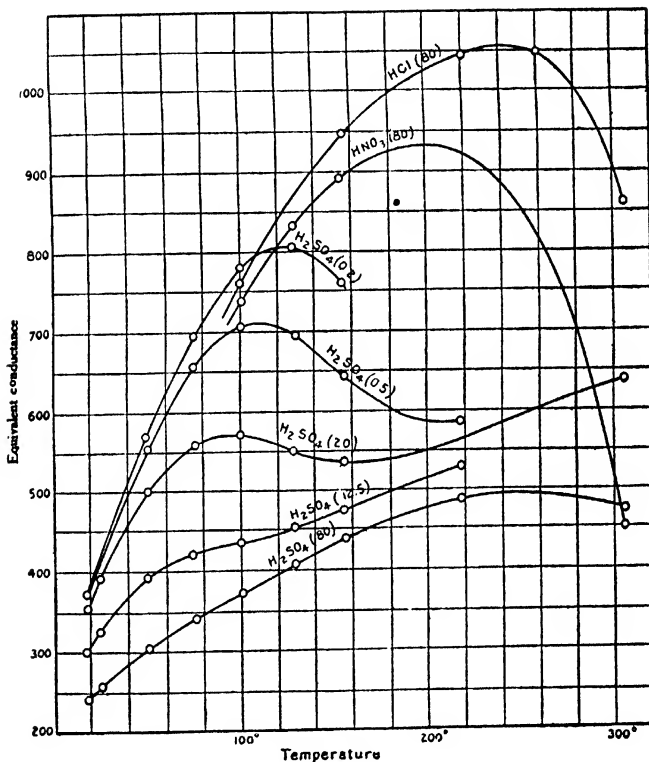

FIG. 16. — EQUIVALENT CONDUCTANCE AND TEMPERATURE

the increase in equivalent conductance is roughly of the same magnitude as the increase in the fluidity of water and is therefore probably due to the decreased resistance to the motion of ions through water. This is illustrated in Figure 16.[1] It will be

[1] Noyes and Coolidge, Carnegie Publication No. **63**, pp. 47 and 55 (1907).

noticed that the rate of increase in conductance becomes less as the temperature increases; this is due to the decrease in dissociation with increasing temperature. At higher temperatures this may more than counterbalance the effect of increased fluidity of water. Thus the equivalent conductance of 0.08 in hydrochloric, nitric, and sulfuric acids all pass through maximum values above 200° C., after which the temperature coefficient is negative.[1] For normal phosphoric acid the temperature coefficient is negative above 74° C., and for normal hypophosphorous acid above 54°.[2]

The temperature coefficients at room temperature, defined by the expression $\dfrac{1}{\kappa_{18}}\left(\dfrac{d\kappa}{dt}\right)_{22}$ [3] for dilute salt solutions are in general around 0.022, for acids about 0.015, and for bases about 0.020.[3]

Conductance and Pressure. — Pressure affects the electrical conductance of solutions in four different ways:[4] the volume change of the solution due to pressure change, the change in mobility of the ions due to the viscosity change in the solution, the change in the ionization of the electrolyte, and the change in the conductance of the solvent medium. The conductance of the medium is usually due to a small impurity of electrolyte. For strong binary electrolytes the effects of change in ionization and in the conductance of the solvent are practically negligible in dilute solution. At room temperature such solutions first decrease in resistance as the pressure increases and then increase. The higher the temperature the sooner the minimum occurs, and the same is true for increase in concentration. For higher concentrations, such as 5-normal sodium chloride, the resistance begins to increase at once, and at 3000 kg./sq. cm. is 8.5 percent higher than at 1 kg./sq. cm. In the case of weak electrolytes the change in dissociation with pressure becomes of appreciable effect on the conductance, and at intermediate concentrations and low temperatures these first three terms are all of the same sign and tend to reduce the resistance. Thus the resistance of 0.01-*n* acetic acid in water at 20.14° has only 0.41 as much resistance at 4000

[1] Noyes and Eastman, Carnegie Publication No. 63, p. 266 (1907).

[2] Arrhenius, *Electrochemistry*, p. 198 (1902).

[3] Tables, Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte*.

[4] Tammann, Z. phys. Ch. **27**, 457 (1898); Kraus, *The Properties of Electrically Conducting Systems*, p. 126.

kg./sq. cm. as at 1 kg./sq. cm.   Since there is usually a decrease
in volume with the formation of ions, an increase in pressure will
increase ionization, as required by Le Chatelier's rule.

Dissociation and Temperature. -- The dissociation of dissolved
electrolytes decreases with an increase in temperature, as is shown
in Figure 17.[1]   It will be noticed that the rate at which ionization
falls off is greater the higher the temperature.   The decrease in
ionization is probably due partly to the decrease in dielectric
constant of water, which falls from 81.3 at 18° C. to 58.1 at 100°.
Another cause for the decrease in ionization is the fact that in
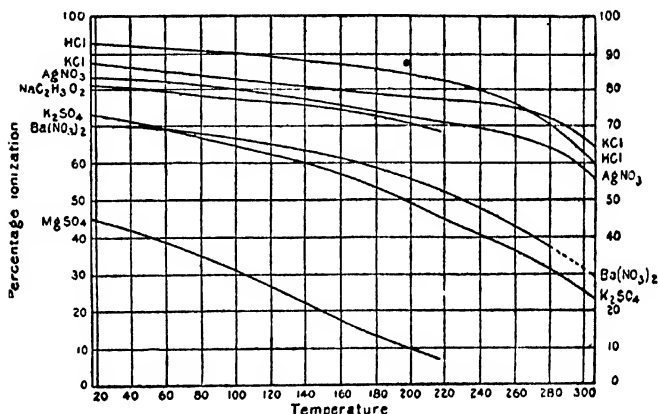
FIG. 17. — IONIZATION AND TEMPERATURE

general when ions unite to form molecules heat is absorbed, and
from this fact and Le Chatelier's principle, a decrease in ionization
with a rise in temperature would take place.   The general state-
ment of this principle, also known as the Principle of Mobile
Equilibrium, is as follows : *When a factor determining the equilib-
rium of a system is altered, the system tends to change in such a way
as to oppose and partly annul the alteration in the factor.*   Thus when
the temperature is increased, the reaction goes in the direction
which absorbs heat.   This principle, like the first and second laws
of thermodynamics, is a matter of experience and no proof has been
given for it.

[1] Noyes, Carnegie Publication No. **63**, p. 339 (1907).

Ostwald's Dilution Law. — If the mass action law is applied to the dissociation of an electrolyte dissociating into univalent electrolytes according to the equation $AB = A^+ + B^-$, we have: the ionization or equilibrium constant $k = \dfrac{(A^+)(B^-)}{(AB)}$, where the parentheses signify concentrations of the inclosed substances. If dissociation is determined by the conductance ratio Λ/Λ_0 and v is the number of liters in which one gram equivalent is dissolved, this reduces to

$$k = \frac{\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)v} \tag{6}$$

The special case of the mass action law applied to the ionization of electrolytes is called *Ostwald's dilution law.*

It is found that this law holds accurately for weak electrolytes, *e.g.* organic acids, that is, those which are only slightly ionized, up to concentrations lying between $v = 16$ and $v = 32$ liters; beyond this limit the constant begins to decrease.[1] The dilution law is illustrated in Table 9.[2]

TABLE 9. IONIZATION CONSTANT FOR ACETIC ACID AT 25° C.

VOLUME CONTAINING ONE EQUIVALENT	Λ	$k \times 10^5$
0.989	1.443	1.405
1.977	2.211	1.652
3.954	3.221	1.652
7.908	4.618	1.814
15.816	6.561	1.841
31.63	9.260	1.846
63.26	13.03	1.846
126.52	18.30	1.847
253.04	25.60	1.843
506.1	35.67	1.841
1012.2	49.50	1.844
2024.4	68.22	1.853
	379.9	

The dissociation constant k is a measure of the strength of acids and bases. For example, mono-chlor, di-chlor, and tri-chlor acetic

[1] Wegscheider, Z. phys. Ch. **69**, 603 (1909).
[2] Kendall, Medd. Vetenskapsakad. Nobelinstitut, **2**, No. 38, p. 1 (1913).

acids are progressively stronger acids and their constants are as follows:

acetic acid	0.0018×10^{-2}
mono-chlor acetic acid	0.155×10^{-2}
di-chlor acetic acid	5.14×10^{-2}
tri-chlor acetic acid[1]	121

The above dilution law also holds for strong electrolytes below 0.0001 normal, as shown in Table 10.

TABLE 10. IONIZATION CONSTANT OF KCl AT 18° C.

Washburn, J. Am. Ch. Soc. **40**, 150 (1918); Weiland, ibid. **40**, 131 (1918).

NORMALITY	$k = \dfrac{\gamma^2 c}{1-\gamma}$
0.00001	0.020
0.00005	0.020
0.00010	0.021
(0.001)	(0.046)
(1.0)	(2.3)

At higher concentrations k increases rapidly and the dilution law fails entirely as shown in the last two lines of this table. The last line is calculated from Table 5.

The mass action law is exact only for perfect gases or perfect solutes, but holds reasonably true for most gases at from 1 to 5 atmospheres and in the case of solutes with electrically neutral molecules up to about 1 molal.[2] For ions, however, there are large deviations even at 0.1 molal concentration. These are therefore not perfect solutes and their mass actions must be expressed by *activities*, a, by which is meant that quantity which, when substituted for the concentration of the substance in mass action equations, expresses its effect in determining equilibrium. It is for this reason that the dilution law does not hold for strong electrolytes, except at great dilutions. The factor by which the concentration must be multiplied to give the activity is called the activity coefficient, α, so that $a = \alpha c$.

A number of empirical formulæ for strong electrolytes have been proposed to take the place of the Ostwald dilution law. One which holds between 1/10000 normal and 1/5 normal and over a wide temperature range is $c(1 - \gamma) = k(c\gamma)^n$, where n is a constant for each electrolyte and lies between 1.43 and 1.56. k is another

[1] Nernst, *Theoretische Chemie*, 8–10 ed., p. 583 (1921).
[2] Noyes and Sherrill, *Chemical Principles*, p. 169 (1922).

constant, and c is the concentration of the electrolyte.[1] *This formula holds independently of the number of ions into which the salt dissociates.* The following formula containing three constants proposed by Kraus and Bray has been found to hold for a variety of binary electrolytes in water and also in other solvents:[2]

$$\frac{(c\gamma)^2}{c(1-\gamma)} = k + D(c\gamma)^m .$$

This takes account of the fact that at high dilutions the mass action law holds, for then $D(c\gamma)^m$ becomes negligible compared to k.

Ionization of Water. — The fact that the purest water obtainable has a small conductance shows that water itself is ionized. The specific conductance of the most carefully purified water was found by Kohlrausch and Heydweiller to have the following values:[3]

Temperature, Degrees C.	Specific Conductance, Mhos / Cm. Cube
0	0.01×10^{-6}
18	0.038×10^{-6}
25	0.058×10^{-6}
50	0.17×10^{-6}

The degree of ionization may be calculated as follows: since, at 25° one centimeter cube has a conductance of 0.058×10^{-6} mho, one liter between electrodes one centimeter apart would have a conductance of 0.053×10^{-3} mho. But if there were one equivalent of hydrogen and hydroxyl ions in one liter, their conductance would be $350 + 192 = 542$ mhos. Therefore the quantity actually present is $0.058 \times 10^{-3}/542 = 1.07 \times 10^{-7}$ equivalent per liter. Entirely different methods give values not more than 20 percent different from this, which is one of the most striking evidences of the ionic theory.[4] Water is exceptional in that its ionization increases with the temperature, because the production of hydrogen and the hydroxyl ions from water is attended by an *absorption* of heat. Usually ionization is attended by an evolution of heat.

Water having a specific conductance of 10^{-6} mho or less cannot be kept in glass for more than a few hours, because it dissolves

[1] Noyes, Carnegie Publication No. **63**, p. 269 (1907).
[2] J. Am. Ch. Soc. **35**, 1315 (1913).
[3] Ann. d. Phys. **53**, 209 (1894); Heydweiller, Ann. d. Phys. **28**, 503 (1909).
[4] Noyes and Kanolt, Carnegie Publication No. **63**, p. 297 (1907).

salts from the glass, and if exposed to the air, dissolves carbonic acid and ammonia. "Conductivity water" should not have a specific conductance greater than 10^{-6} mho and therefore must be freshly prepared by redistilling ordinary distilled water after adding some alkaline permanganate solution. In determining the conductance of dilute solutions the specific conductance of the water is subtracted from that of the solution to get the conductance of the dissolved salt. This is called the water correction.

Heat of Neutralization. — When a highly dissociated base is neutralized by a highly dissociated acid by mixing dilute solutions of the two, according to the dissociation theory nothing takes place except the union of hydrogen and hydroxyl ions to form water:

$$B^+ + OH^- + A^- + H^+ = B^+ + A^- + H_2O.$$
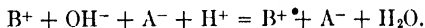
This is in agreement with the fact that any strong base neutralized with any strong acid in dilute solution gives the same heat effect, 13,780 cal. for one gram-mol of water at 18° C.[1]

Solubility Product Law. — When a slightly soluble binary electrolyte in the solid state is in contact with its saturated solution, there is an equilibrium with respect to the two reactions: AB solid $= AB$ dissolved and AB dissolved $= A^- + B^+$, and the mass action law requires that the concentration of the dissolved, undissociated substance should be constant and that $(A^-)(B^+)/(AB) = k_1$ and since (AB) is constant, $(A^-)(B^+) = k_2$. If C_0 is the solubility in gram-mols per liter and γ_0 the dissociation of the saturated solution, $(A^-) = (B^+) = \gamma C_0$ and therefore $(\gamma C_0)^2 = k_2$. This is called the *solubility product law* and may be stated as follows: In the saturated solution of a slightly soluble uni-univalent salt, the product of the concentrations of the kinds of ions into which the salt dissociates is constant. The presence of other ions must be taken into account. Suppose an electrolyte having a common ion A with a slightly soluble salt AB is added to a saturated solution of AB; the concentration of the ion A will be increased, consequently that of B must decrease in order to keep the value of the product constant, and this takes place by a certain quantity of B uniting with A to form undissociated AB and precipitating. This is illustrated by the results in Table 11.[2]

[1] Lewis and Randall, *Thermodynamics*, p. 486 (1923), where data by Wörmann, Ann. d. Phys. **18**, 775 (1905), are summarized in the equation $\Delta H = 29,210 - 53\ T$. ΔH therefore varies considerably with the temperature. See also Richards and Rowe, J. Am. Ch. Soc. **44**, 684 (1922).

[2] Noyes, Z. phys. Ch. **6**, 246 (1890).

<div align="center">

TABLE 11

SOLUBILITY OF AgBrO₃ IN THE PRESENCE OF AgNO₃ AND OF KBrO₃

</div>

GRAM-MOLS OF ADDED SALT	SOLUBILITY OF AgBrO₃ IN PRESENCE OF		SOLUBILITY CALCULATED FROM SOLUBILITY PRODUCT LAW
	AgNO₃	KBrO₃	
0.	0.00810	0.00810	———
0.0085	0.00510	0.00519	0.00504
0.0346	0.00216	0.00227	0.00206

Suppose the added salt has the concentration x gram-mols per liter and the dissociation γ_1 while AB has the dissociation γ, the equation then becomes

$$C\gamma(C\gamma + x\gamma_1) = (C_0\gamma)^2, \qquad (7)$$

where C is the concentration of the saturated solution of AB in the presence of the added salt.

Though strong electrolytes do not obey the mass action law except below 1/10000 normal, it has been found that many slightly soluble salts obey the solubility product law approximately up to concentrations of 0.1 to 0.2 equivalent per liter.[1] The product of the ion concentrations is, however, not strictly constant but generally increases with the concentration of the added salt.

On the other hand, the concentration of the un-ionized substance is in no case constant as required by the mass action law, but decreases rapidly with increasing concentration of the added salt.[2] The addition of small amounts of a salt with no common ion increases the solubility of the slightly soluble salt because of the formation of other undissociated compounds. If potassium sulfate, for example, is added to a solution of thallous chloride, thallous sulfate and potassium chloride will be formed, and more thallous chloride will go in solution to keep the product of its ions constant.[3]

When the attempt is made to apply this law to uni-bivalent salts, the irregular variation in the concentration of the un-ionized part, the abnormal increase in the solubility product, and the ab-

[1] Noyes and Sherrill, *Chemical Principles*, p. 167 (1922).
[2] Bray, J. Am. Ch. Soc. **33**, 1083 (1911).
[3] Bray and Winninghoff, J. Am. Ch. Soc. **33**, 1671 (1911).

normal form of the solubility curve for the addition of the common bivalent ion lead to the assumption that all uni-bivalent salts dissociate in two steps, forming such intermediate ions as KSO_4^- and $BaNO_3^+$.[1]

Ionization of Electrolytes in Mixtures. — If equal volumes of solutions of two electrolytes are mixed and the specific conductance determined, it will in general be found that the specific conductance of the mixture is not equal to the mean of the conductances of the two solutions, but is somewhat less. This is due to the formation of other molecules than those which existed in either solution before mixing, for if potassium nitrate and sodium chloride solutions are mixed, there will be formed some undissociated sodium nitrate and potassium chloride. If the electrolytes are weak and the mass action law applies, the concentration of each ion could be calculated from a knowledge of the dissociation constants and the original concentrations of the electrolytes, and from these results the specific conductance of the mixture.[2] If the mass action law does not apply, one of the empirical formulas given above would be required. The mathematical difficulties involved in this calculation, however, would be very great.

If the two salts have a common ion, the calculation is simplified by the *rule of isohydric solutions* discovered by Arrhenius. This rule may be stated in the following more convenient form than that given by Arrhenius, without much loss in accuracy: *The dissociation of each salt in the mixture is just as great as the dissociation of each salt would be alone if its equivalent concentration were equal to the total equivalent concentration of both salts in the mixture.* An analogous rule may be used for a mixture of any number of salts, all having a common ion.[3] In case the concentrations of the common ion in the two solutions before mixing are equal, there will be no change in dissociation in mixing in any proportions, and the specific conductance of the mixture will be the mean of the specific conductances of its components. Such solutions are called *isohydric*.

Problem 3. Calculate the specific conductance of a solution made by mixing equal volumes of 0.1-n potassium chloride and 0.05-n sodium chloride. For the necessary data see Table 6.

Solution. — Find total concentration of salts after mixing and the dissociation of each by interpolation. Then the conductance

[1] Harkins, J. Am. Ch. Soc. **33**, 1871 (1911).
[2] Nernst, *Theoretische Chemie*, p. 586 (1921).
[3] Arrhenius, *Theory of Solutions*, p. 136 (1913).

of the KCl contained in one centimeter cube is the product of the amount in equivalents contained by the dissociation by the conductance at infinite dilution. The conductance of the sodium chloride is obtained in the same way, and the desired result is the sum of the two conductances.

Conductance of Non-aqueous Solutions. — Up to the present time solutions in other solvents than water have not attained any importance in applied electrochemistry, though they have great theoretical importance. The following are some of the non-aqueous solvents that have been investigated: liquid ammonia, liquid sulfur dioxide, various alcohols, mixtures of alcohols and water, pyridine, acetone, anhydrous formic acid, and liquid hydrocyanic acid. The conductances of ions in non-aqueous solutions are in general of the same order of magnitude as in water, but somewhat less numerically. Hydrocyanic acid solutions in some cases conduct better than the corresponding water solutions, corresponding to this acid's higher dielectric constant of 96. According to Carrara and Walden the general statement may be made that the electrolytic dissociation theory applies as well to non-aqueous as to aqueous solutions.[1] Another general statement which may be made is that for any given salt in most solvents between $0°$ and $50°$ C. the values of $\Lambda_0\eta_0$ are constant.[2] Solutions of alkaline metals in liquid ammonia are particularly interesting because they are the only known solutions that have both electrolytic and metallic conduction. Very dilute solutions conduct electrolytically, and as the concentration increases metallic conduction takes place simultaneously with electrolytic; with concentrated solutions the conductance is entirely metallic. The explanation is as follows. In these solutions the positive ion is identical with the positive ion of a dissolved salt of the same metal while the negative ion is apparently the negative electron. At low concentrations the electron is associated with ammonia and its speed is therefore of the order of magnitude of ordinary ions, but when the concentration increases the electron loses ammonia and its speed becomes comparable to that of electrons in metals.[3]

Conductance of Fused Salts. — In general fused salts, hydrates, and oxides are good conductors of electricity. Equivalent conductances may be calculated from specific conductances if the

[1] Arrhenius, *Theory of Solutions*, p. 152 (1913).
[2] Walden, Z. phys. Ch. **55**, 246 (1906); Z. anorg. Ch. **113**, 85 (1920).
[3] Kraus, *The Properties of Electrically Conducting Systems*, p. 367 (1922).

density of the fused substance is also known. Equivalent conductances of fused salts are of about the same order of magnitude as the equivalent conductance of the salt at infinite dilution in water. Table 12 gives some examples.[1]

TABLE 12. SPECIFIC AND EQUIVALENT CONDUCTANCES OF FUSED SALTS

SALT	TEMP., DEG. C.	SPC COND, κ	EQUIVALENT VOL v, IN CC	EQUIVALENT COND $= \kappa v$	Λ_0 IN AQUEOUS SOLUTION AT 18° C.
NaNO$_3$	305 m. p.	0.9510	41.32	42.15	105.2
	400	1.384	45.95	63.59	
	500	1.716	47.75	81.94	
KNO$_3$	333.7 m. p.	0.6225	53.96	33.59	126.3
	400	0.8255	55.41	45.74	
	500	1.109	57.75	64.04	
AgNO$_3$	218 m. p.	0.6815	42.88	29.22	115.8
	300	1.049	43.89	46.16	
KCl	943.5	2.954	6.21	154.6	130.0
Na$_2$MoO$_4$	1408	2.403	8.719	105.3	
Na$_2$WO$_4$	1501	2.453	8.469	110.7	

The equivalent conductance is in general nearly linear with respect to the temperature and increases at about the same rate as the fluidity.

The equivalent conductance of mixtures of fused salts can in some cases be expressed as the mean of the conductances of the components. This holds for mixtures of sodium and potassium chlorides and of calcium and strontium chlorides,[2] but the equivalent conductance of a mixture of sodium and potassium nitrates is less than that calculated from those of the components. The equivalent conductance of a mixture of two salts is calculated by the formula,

$$\Lambda = \frac{\kappa(n_1 M_1 + n_2 M_2)}{d(n_1 + n_2)} \tag{8}$$

where κ is the specific conductance of the mixture, d the density, and n_1 and n_2 the number of gram-mols of each salt of molecular weights M_1 and M_2 in the mixture. The mean of the equivalent

[1] Goodwin and Mailey, Phys. Rev. **26**, 28 (1908); Jaeger and Kampa, Z. anorg. Ch. **113**, 27 (1920).

[2] Arndt, Z. Elektroch. **13**, 509 (1907).

conductances of two salts is calculated from the equivalent conductances Λ_1 and Λ_2 of the pure salts by the equation:

$$\Lambda = \frac{n_1\Lambda_1 + n_2\Lambda_2}{n_1 + n_2} \tag{9}$$

When a highly conducting salt is dissolved in a poorly conducting one, a mixture of high equivalent conductance is obtained, just as when a salt is dissolved in water. Fused mercuric chloride is a poor conductor, but the addition of potassium, sodium, cæsium, or ammonium chlorides produces well-conducting mixtures. These solutions differ from aqueous solutions in that the equivalent conductances of the dissolved salts decrease with dilution. These appear to form complexes with the solvent probably according to the reaction: [1]

$$2\,MCl + HgCl_2 = M^+ + MHgCl_4{}^-.$$
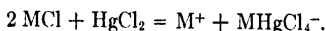
A second example of more practical importance is that fused cryolite, $3\,NaF \cdot AlF_3$, which is a poor conductor, forms well-conducting solutions with aluminum oxide.

Nothing definite can be said concerning the extent of ionization of fused salts, though it is generally believed that they are highly ionized and that there is little if any change in ionization with temperature. The results of crystal structure determinations favor the view that ionization is complete even in the solid state. Melting would therefore merely make it possible for the already existing ions to move.

Salts begin to conduct a little before the melting point is reached, but the conductance increases rapidly at this point, on account of the sudden increase in fluidity.

Problem 4. Suppose a sample of water contains 11.6 parts of sodium chloride and 17 parts of sodium nitrate per million. What is its approximate resistance per centimeter cube at 18° C.? See Table 5. *Ans.*, 23,000 ohms.

Problem 5. The equivalent conductance of 0.01-n-KCl is 122 reciprocal ohms. What is its specific resistance?

Problem 6. From Table 5 calculate the degree of ionization of NaCl, AgNO₃, and CuSO₄ at normal concentration.

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CHAPTER IV

ELECTRO-OSMOSIS — ELECTROCHEMISTRY OF COLLOIDS

Definitions. — It was found by Reuss of Moscow in 1807 that if a porous diaphragm, such as parchment, animal membrane, or unglazed burnt clay, completely separates a liquid into an anode and a cathode portion, liquid is transferred from one side of the diaphragm to the other when a voltage is applied. The same happens if the diaphragm consists of capillary tubes or a finely powdered substance suitably held in position, for example by placing at the bottom of a U-tube. This is called *electro-osmosis* or *electro-endosmose*.

Direction of Motion. — The direction in which this transfer takes place depends both on the liquid and on the diaphragm material. Distilled water is found to move to the cathode for most substances, including silk, linen, ivory, sand, burnt clay, glass, graphite, iron filings, spongy platinum, sulfur, and wood,[1] while it moves to the anode through diaphragms of carborundum, asbestos, cotton, wool, chromium chloride, aluminum oxide, cobalt oxide, zinc oxide, and barium carbonate.[2]

Dielectric Constant and Electro-osmosis. — Perrin[3] finds that only those liquids having high dielectric constants (over 20) show marked electro-osmosis, while those of low constants (below 5) do not. Those which show electro-osmosis with all diaphragms include water, ethyl and methyl alcohols, acetone, acetylacetone, and nitrobenzene, while those not showing it with any diaphragm are chloroform, ether, petroleum, benzene, turpentine, and carbon bisulfide. Quincke, however, found turpentine moved to the anode through all diaphragms except sulfur.

Wiedemann's Laws. — Wiedemann was the first to study this phenomenon quantitatively, with the following empirical results:[4]

1. The amount of liquid transferred in a given time through a

[1] Quincke, Pogg. Ann. **107**, 1 (1859); **110**, 38 (1860).
[2] Freundlich, *Kapillarchemie*, p. 232 (1909).
[3] J. Chim. Phys. **2**, 601 (1904).
[4] See *Die Lehre von der Elektricität*, **1**, 993 (1893).

porous diaphragm is proportional to the current, and is independent of the area and thickness of the diaphragm; that is, the amount transferred $= k \cdot I$.

2. For a given diaphragm the difference in hydrostatic pressure maintained on the opposite sides is proportional to the potential difference of the two sides and is independent of the dimensions of the diaphragm, that is height of liquid $= k' \cdot E$.

It has been found more recently that the equation, water transferred $= kI$, holds only up to a limiting current density at the diaphragm and that the amount of liquid transferred is also dependent on the temperature.[1] For distilled water and Pukall clay as diaphragm the constant k passes a maximum point as the current is increased and for a constant current the amount of water transferred reaches a maximum at between 35° and 40° C. The maximum occurs at different temperatures for different substances, and no maximum is found for distilled water with diaphragms of alundum or of silicon carbide. For these diaphragms the quantity of liquid transferred increases steadily but more slowly than the fluidity.[2]

Comparison between Electro-osmosis and Evaporation. — If a given amount of coal were used to generate electricity by a steam engine and dynamo and remove water by electro-osmosis, it would remove 45 times as much as if used for evaporation, if electro-osmosis is carried out at the maximum point of efficiency. Comparing with Faraday's law, 1000 times as much passes through the diaphragm as is electrolyzed.[3]

Helmholtz's Explanation of Electro-osmosis. — Electro-osmosis was explained by Helmholtz on the assumption that there is an electric double layer at the boundary of the moving liquid and a thin liquid film held stationary at the surface of the capillary. If a potential gradient is impressed from without, the charged liquid is forced to move, or if the liquid is forced through the tubes by mechanical means, the charge is carried and a current is produced.[4]

If a force f acts tangentially on a unit surface of a liquid and causes it to move with a velocity v by another surface at a perpendicular distance d, then,

[1] Cruse, Phys. Zeitschr. **6**, 201 (1905).

[2] Briggs, Bennett, and Pierson, J. Phys. Ch. **22**, 256 (1918).

[3] Cruse, *l.c.*

[4] For the following mathematical derivations, see Perrin, *l.c.* and Freundlich, *Kapillarchemie*, p. 226 (1909).

$$f = \frac{\eta v}{d},$$

where η is the viscosity coefficient. If ρ is the electric charge per unit of area of one side of the double layer, the force acting on unit area of the movable side of the double layer is ρH, where H is the potential gradient. Therefore

$$\rho H = \frac{\eta v}{d}.$$

Also, the volume of liquid ϕ moving by a given point in the capillary in unit time is $\phi = \pi r^2 v$, where r is the radius of the capillary. Eliminating v gives the equation,

$$\rho d = \frac{\eta \phi}{\pi r^2 H}.$$

If D is the dielectric constant and ϵ is the potential difference between the movable and the fixed faces of the double layer, then

$$\epsilon = \frac{1}{D} 4 \pi \rho d,$$

since the electric force between the two layers is $4 \pi \rho / D$ (the work necessary to move unit charge from one surface to the other is $4 \pi \rho d / D$ which by definition is potential difference). By substituting the value of ρd in the last equation the value of ϕ is found to be,

$$\phi = \frac{D r^2 H \epsilon}{4 \eta} = \frac{D \pi r^2 E \epsilon}{4 \pi \eta l}, \tag{1}$$

where $H = E/l$, E being the applied voltage and l the length of the capillary. By substituting for E its equivalent iR and $R = l/k\pi r^2$, where κ is the specific conductance of the liquid filling the capillary, the following equation results:

$$\phi = \frac{\epsilon i D}{4 \pi \eta \kappa}, \tag{2}$$

which shows that if the current is kept constant, the amount of liquid carried through capillaries is independent of their cross-section or length, as found experimentally by Wiedemann.

If the liquid is not allowed to flow, but is balanced by an equal hydrostatic pressure, this must be large enough to carry in the opposite direction the liquid moved by the electric forces. By Poiseuille's rule this pressure is given by the equation:

$$\phi = \frac{\pi P r^4}{8 \eta l},$$

where P is the hydrostatic pressure causing the flow of ϕ cc. of liquid per second. Substituting this value of ϕ in equation (1) gives,

$$P = \frac{2 \epsilon D E}{\pi r^2}, \tag{3}$$

which shows the pressure is proportional to the applied electromotive force, as stated in Wiedemann's second law, and inversely proportional to the square of the diameter of the capillary, as found by Quincke.

If ϕ is determined, ϵ, the difference in potential of the double layer, can be calculated. The value of ϵ for glass and water calculated by Freundlich from Quincke's results by formula (2) is 0.05 volt. Formula (3) could also be used for calculating ϵ.

These deductions do not explain Cruse's results mentioned above, nor does he offer any satisfactory explanation.

Sign of Charge. — With regard to the sign of the charge, the empirical rule has been found, that non-conductors of high dielectric constants are charged positively when brought in contact with those of low constants. This is in many cases a quantitative relation. If the potential difference between different liquids and glass is measured by the height to which these liquids rise in the same glass capillary under the same potential gradient, the following relation between differences in potential and dielectric constants was found to hold for twenty-seven liquids:

$$\frac{h_1}{h_2} = \frac{D_1 - D \text{ glass}}{D_2 - D \text{ glass}}.$$

This law is evidently not general, for if it were, water would always migrate to the cathode, which is not the case.

Diaphragm Current. — If a liquid is forced through capillaries by mechanical forces, an electric *diaphragm current* is produced. For positively charged liquids the current is of course in the direction of liquid flow. If the diameter of the capillary is so small that Poiseuille's law holds, the electromotive force is proportional to the force applied, is independent of the dimensions of the capillary, and is given by the formula [1]

$$E' = \frac{D \epsilon P}{4 \pi \eta \kappa}, \tag{4}$$

[1] Perrin, J. Chim. Phys. **2**, 611 (1904).

where the letters have the same significance as above. This electromotive force amounts to about ten volts when water is forced through sulfur capillaries with a pressure of one atmosphere.

It was shown by Saxén[1] that formula (2) for the quantity of liquid transferred by an externally applied electromotive force and formula (4) giving the electromotive force produced by an externally applied mechanical pressure are in agreement. Equations (2) and (4) may be put in the forms

$$\frac{\phi}{i} = \frac{\epsilon D}{4\pi\eta\kappa} \text{ and } \frac{E'}{P} = \frac{\epsilon D}{4\,\pi\eta\kappa}, \text{ and therefore } \frac{\phi}{i} = \frac{E'}{P}.$$

These quantities were measured in the same apparatus, using a clay diaphragm and dilute solutions of zinc, copper, and cadmium sulfates, and it was found that the relation holds true to about one percent.

Coehn's empirical law for the charge on two substances when brought in contact does not hold at all for aqueous solutions. The present theory is that the charge on the diaphragm depends on the relative adsorption of cation and anion. If the diaphragm adsorbs the cation to a greater extent than the anion, it becomes positively charged and the liquid moves to the anode. Ions of the opposite sign tend to neutralize this charge, and this effect increases rapidly with the valence of the ion. In many cases a reversal in the direction of migration of the liquid takes place when the solution is alkaline in place of acid, since every diaphragm tends to be charged positively in acid solution and negatively in alkaline.[2]

Cataphoresis. — If the material of a diaphragm in which the liquid moves to the cathode is pulverized and suspended in this liquid, the suspension moves to the anode. This action is called *cataphoresis*, though this expression is also used synonymously with electro-osmosis. The velocity of migration of suspended particles is of the same order of magnitude as that of ions, and there seems to be no difference in kind between cataphoresis and ionic migration.[3]

Similarly, if finely divided charged particles fall by gravity through a liquid, a current is produced in the expected direction.[4]

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[1] Wied. Ann. **47**, 46 (1892).
[2] Bancroft, *Colloid Chemistry*, p. 209.
[3] McBain, Brit. Ass. Adv. Sci., 1920, appendix, p. 3.
[4] Billiter, Ann. d. Phys. **11**, 937 (1903). This, however, was not confirmed by Whitney and Blake, J. Am. Ch. Soc. **26**, 1378 (1904).

Electrostenolysis takes place when a current is sent through an electrolyte contained in very minute capillaries. Cracks made by suddenly cooling a heated glass tube by dipping in water are suitable for showing this effect. If a current is forced through these capillaries containing a metallic salt solution, metal is deposited in the capillaries and gas is evolved, if the current is above a certain critical value depending on the electrolyte. There is at present no satisfactory explanation of this phenomenon.

Colloids. — As the size of the particles of a dispersed system is reduced, we pass from suspensions to colloids and finally to molecules of crystalloids. A sharp break occurs between $0.1\,\mu$ and $1.0\,\mu$ in the properties of the particles as regards the Brownian movement, forming sediment, and passing through filter paper. The limit of the resolving power of the best microscopes is also in this region, being about $0.2\,\mu$. (μ = one micron = 10^{-3} mm.; $\mu\mu = 10^{-6}$ mm.)

The sizes of particles in these different states is roughly as follows: [1]

Suspensions: particles down to about $0.1\,\mu$.

Hydrosols (colloidal solutions and turbidities): $0.001\,\mu$ to $0.1\,\mu$.

Molecules of crystalloids: $0.1\,\mu\mu$ to $1.0\,\mu$.

Hydrosols diffuse and have osmotic pressure and in general are more like crystalloids than suspensions. The property of a dispersed system is, however, not dependent alone on the size of the particles, but also on the solvent. In general a system may be considered colloidal if the effect of gravity is negligible compared with other forms of energy.

This criterion gives a means of determining whether a substance is a colloid or not, but there is no such simple classification of colloids themselves. In order to distinguish between substances of the type of colloidal gold and egg albumin, the division into *colloidal suspensions* and *colloidal solutions* has been proposed. In place of colloidal suspension, the following names have been suggested: *hydrophobic colloids, lyophobic colloids, suspension colloids,* or *suspensoids,* while the following terms are used synonymously with colloidal solutions: *hydrophiles, lyophile colloids, emulsion colloids,* and *emulsoids.* While this classification distinguishes between widely different kinds of colloids, it is not a satisfactory means of classification, as many colloids could be placed in either group.

[1] Zsigmondy, *Chemistry of Colloids*, p. 20 (1927).

Another classification depends on their behavior in the dry state; they may be reversible or irreversible. Irreversible colloids when coagulated can be brought back to the colloidal state again only by electrical or chemical energy; reversible colloids dissolve to form an apparently homogenous hydrosol. In this class belong gum arabic, albumin, glue, and gelatin.

Suspension colloids, consisting of substances practically insoluble in the dispersing medium, such as colloidal gold, may be prepared either by a suitable chemical reaction which produces the dispersed phase in the dispersing medium, or by grinding in the presence of the dispersing medium, or, in the case of metals, by striking an arc between electrodes consisting of the metal to be reduced to the colloidal state while submerged in the liquid. From 4 to 10 amperes and 30 to 40 volts are required.

Emulsion colloids, whose solutions have the power of gelatinizing, such as glue and albumin, frequently dissolve when brought in contact with the dispersing medium, especially at higher temperatures.

When colloidal particles coalesce and precipitate, the precipitate is called a gel. If the dispersing medium is water, it is called a hydro-gel, and similar prefixes are used for other media. The change back from a gel to a sol is called *peptization*. This is often assisted by the presence of a small amount of some peptizing agent; for example, silver nitrate peptizes a precipitate of silver iodide.

Colloid particles, like suspensions, are generally charged; the origin of the charge may be due to (1) dissociation, as with electrolytic colloids such as dyestuffs with high molecular weights and soap solutions; [1] (2) in the case of non-conductors, to difference in dielectric constants, and (3) to adsorption or to giving off of ions to the liquid. Small particles of metals may give off ions just like little electrodes, leaving the metal particles negatively charged, and the noble metals may contain free hydrogen and give off hydrogen ions like a hydrogen electrode.

The charges on suspension colloids are the principal cause of their remaining in a fine state of division,[2] though the Brownian movement also helps, and possibly also a small value of surface tension. Electric forces are much less important for emulsion colloids, because of the small surface tension.

The sign of the charge on colloids is largely dependent on the electrolytes present. Hydrogen and hydroxyl ions are especially

[1] McBain, *l.c.*
[2] Ellis, Z. phys. Ch. **89**, 145 (1914).

important. Albumen, for example, has no charge in pure water, while a trace of alkali causes it to migrate to the anode and a trace of acid to the cathode. The same holds true for many suspended powders and hydrosols. Table 13 shows the charge on colloidal particles when prepared in the usual way and purified by dialysis.[1]

TABLE 13. CHARGE ON COLLOIDAL PARTICLES

CHARGE POSITIVE, MIGRATE TO CATHODE	CHARGE NEGATIVE, MIGRATE TO ANODE
Colloidal iron oxide	Colloidal gold, silver, platinum
" cadmium hydroxide	sulfur
" aluminum hydroxide	arsenious sulfide
" chromium oxide	antimonius sulfide
" titanic oxide	cupric sulfide
" thorium oxide	lead sulfide
" zirconium oxide	cadmium sulfide
" cerium oxide	mastic
Basic dyestuffs	gamboge, gum arabic
(colloidal or crystalloidal)	soluble starch
	silicic acid
	stannic acid
	molybdenum blue
	tungsten blue
	vanadium pentoxide
	tannin
	caramel
	hemoglobin
	acid dyestuffs
	(colloidal and crystalloidal)

Even some crystalloidal non-electrolytes, such as sugar, migrate with the current, while others do not.[2]

The rate of migration of colloids is of the same order of magnitude as that of suspensions and ions. Since colloid particles are much larger than ions, it is evident therefore that their charge must be much larger also. It is calculated from Stokes' law that the charge on a silver particle having a diameter of 50 $\mu\mu$ and a velocity of 2 μ per second per volt-centimeter would equal that of 99 chlorine ions.[3]

The electrochemical equivalent has been determined for a number of hydrosols, and is found to be much smaller than that of electrolytes. The electrical conductances of colloidal solutions

[1] Zsigmondy, *Chemistry of Colloids*, p. 45; Bredig, Z. Elektroch., **9**, 738 (1903).

[2] Coehn, Z. Elektroch. **15**, 652 (1909).

[3] Zsigmondy, *l. c.*, p. 51.

have not yet been determined with accuracy, on account of their small values.[1]

According to Loeb[2] the theory of colloidal behavior can be quantitatively explained by means of two laws, the law of stoichiometry and Donnan's theory of membrane equilibria.[3] This theory is stated by Donnan as follows: "We suppose that the membrane (indicated in the following diagram by a vertical line) be impermeable to the anion R of a salt NaR (and also for the non-dissociated part of the salt NaR), but permeable for all other ions and salts to be considered in this connection. . . .

"Suppose that in the beginning we have a solution of NaR on one side of the membrane (indicated by the vertical line) and of NaCl on the other side, o

$$
\begin{array}{c|c}
\text{Na}^+ & \text{Na}^+ \\
\text{R}^- & \text{Cl}^- \\
(1) & (2)
\end{array}
$$
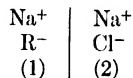
In this case NaCl will diffuse from (2) to (1). In the end the following equilibrium will result:

$$
\begin{array}{c|c}
\text{Na}^+ & \text{Na}^+ \\
\text{R}^- & \\
\text{Cl}^- & \text{Cl}^- \\
(1) & (2)
\end{array}
$$
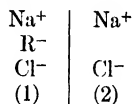
When this equilibrium is established, the energy required to transport isothermally and reversibly 1 gram-molecule Na from (2) to (1) equals the energy which can be gained by the corresponding reversible and isothermal transport of a gram-molecule Cl⁻." That is

$$
\text{RT} \log \frac{(\text{Na}^+)_2}{(\text{Na}^+)_1} + \text{RT} \log \frac{(\text{Cl}^-)_2}{(\text{Cl}^-)_1} = 0,
$$

or

$$
(\text{Na}^+)_2 (\text{Cl}^-)_2 = (\text{Na}^+)_1 (\text{Cl}^-)_1,
$$

where the parentheses signify molar concentrations. Those who wish to follow the consequences of this theory will find it in Loeb's work referred to above.

[1] Duclaux, C. r. **140**, 1468 (1905); Malfitano, C. r. **139**, 1221 (1904); Nernst, *Theoretische Chemie*, 8–10 ed., p. 494 (1921).

[2] *Proteins and the Theory of Colloidal Behavior*, p. 26 (1922).

[3] Z. Elektroch. **17**, 572 (1911).

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CHAPTER V

ELECTROMOTIVE FORCE

Definitions. — Electric energy consists of two factors, quantity of electricity and difference of potential. So far only the first factor has been considered. The present chapter will take up the differences of potential produced by *voltaic* or *galvanic cells*, which may be defined as any arrangement by which the energy of chemical reactions, or of certain physical processes, such as diffusion, is changed to electric energy. The subject of the chapter following will be the voltage that must be applied to *electrolytic cells* to force a current through them.

Measurement of Electromotive Force. — When the capacity of a voltaic cell is sufficient to furnish the current required by a voltmeter connected across its terminals without affecting its electromotive force, a voltmeter reading is the simplest method of determining this quantity. The Poggendorff method, however, is used where the greatest accuracy is required, or where the cell is too easily polarized to allow taking an appreciable current from it. This method depends on balancing the unknown against a known electromotive force. It is illustrated in Figure 18. AB represents a wire stretched on a meter scale, V a two-volt storage battery, C the cell to be measured, D a galvanometer, and K a key. The two cells must be connected so as to oppose each other, though both negative poles could be connected to A. The measurement consists in finding the position on the bridge of the sliding contact D where there is no deflection in the galvanometer when the key is closed. Then if the wire is of uniform resistance throughout,

FIG. 18. — POGGENDORFF METHOD OF MEASURING ELECTROMOTIVE FORCE

the fractional part of the wire AD/AB is that part of the electromotive force of V that equals the electromotive force of C; that is,

$$\frac{AD}{AB} \times \text{e.m.f. of } V = \text{e.m.f. of } C.$$

V is not a standard cell, but only one which should remain constant
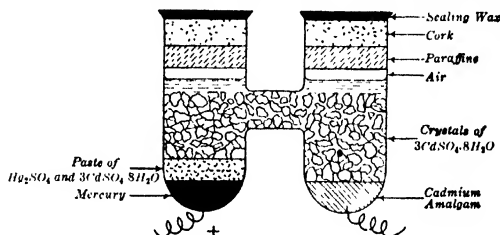
FIG. 19. — WESTON STANDARD CELL

during the measurement. In order to get a comparison with a standard cell C', C is replaced by C' and a new balance found at D'. Then $AD : AD' = \text{e.m.f. of } C : \text{e.m.f. of } C'$.

The apparatus required for these measurements is made in a compact form called a *potentiometer*, in which the slide wire is wound on a drum.

The most commonly used standard cell is the Weston cell, represented in Figure 19. It has an electromotive force represented by the equation : [1]

$$\mathbf{E} = 1.0183 - 0.00004075(t - 20) - 0.000000944(t - 20)^2$$
$$+ 0.0000000098(\, t - 20).^3$$

The small temperature coefficient of this cell is one of its principal advantages.

The Clark cell is as follows :

10 percent zinc amalgam	ZnSO₄.7H₂O crystals in sat. sol. of ZnSO₄	Hg₂SO₄ paste	Hg.
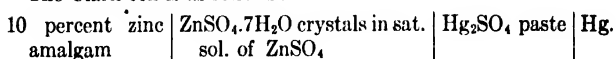
It has the electromotive force

$$\mathbf{E} = 1.4328 - 0.001119(t - 15) - 0.000007(t - 15)^2,$$

and is used to define the practical value of the international volt, as shown in the appendix.

[1] Bull. Bureau of Standards, **5**, 336 (1909) ; Bureau of Standards Report to Int. Committee on El. Units and Standards, p. 206 (1912).

The Helmholtz calomel cell is the following:

Zinc|ZnCl$_2$ sol. sp. gr. 1.409 at 15°|Hg$_2$Cl$_2$ paste|Hg.
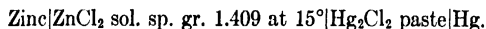
At 15° C. this cell has an electromotive force of 1 volt and a temperature coefficient of + 0.00007 volt per degree.

Reversible and Irreversible Cells. — There are two kinds of voltaic cells, reversible and irreversible. A reversible cell is one in which the original condition can be restored, after taking current from it, by passing the same amount of electricity through the cell in the opposite direction, and by the expenditure of the same amount of energy that was taken from it.

Irreversible cells are those in which this cannot be done. Electromotive forces can be calculated with accuracy only for reversible cells. Volta's cell, consisting of zinc, dilute sulphuric acid, and silver, is an example of an irreversible cell, for on taking current from the cell hydrogen is evolved at the cathode which would not be recovered in sending current through in the opposite direction, and moreover the reverse current would change the silver electrode to silver sulfate.

The Daniell cell, Zn|ZnSO$_4$ sol.|CuSO$_4$ sol.|Cu, is an example of a reversible cell, for the reaction goes in the opposite direction when the current is reversed, and the original state of the cell is restored.

The Gibbs-Helmholtz Equation. — Gibbs and Helmholtz derived independently a relation between the heat liberated in a reaction, the electric energy produced by the voltaic cell in which the reaction is made use of, and the temperature coefficient of the electromotive force of the cell. This relation can be derived by a process similar to the Carnot cycle, as follows.

Let Q represent the heat evolved by the reaction when it takes place without doing any work, and therefore the total energy change of the reaction, and $\mathbf{E}$ the electromotive force of the cell, at the absolute temperature T. The same quantities at $T + dT$ are $Q + dQ$ and $\mathbf{E} + d\mathbf{E}$.

(1) The cell is removed from a reservoir in which it is contained at $T°$ and placed in one at $T + dT$, absorbing k_1dT calories. The cell is now allowed to deliver $\mathbf{F}$ coulombs of electricity, doing the electrical work equivalent to $j(\mathbf{E} + d\mathbf{E})\mathbf{F}$ calories, j being the factor to change joules to calories. According to the first law of thermodynamics,

Decrease in total energy = work done − heat absorbed. (1)

Substituting in the corresponding values,

$$Q + dQ = j(E + dE)F - q,$$

therefore the heat absorbed at $T + dT$ is,

$$j(E + dE)F - (Q + dQ) + k_1 dT.$$

(2) Now cool the cell to $T°$ by placing in the reservoir at this temperature. The heat capacity of the cell after the reaction is k_2 and it therefore gives up the heat $k_2 dT$. (3) Next F coulombs are sent through the cell in the opposite direction. Substituting in equation (1) above,

$$- Q = - jFE - q',$$

therefore $- q'$, the *heat given out* to the reservoir at the lower temperature is $jFE - Q + k_2 dT$. The result of this reversible, cyclical process is that the cell has done the work, equivalent to

$$j(E + dE)F - jFE = jFdE \text{ calories,}$$

and at the same time $jFE - Q + (k_2 - k_1)dT$ calories have fallen through the temperature dT. The third term is entirely negligible in comparison with the first two.

It is shown by the second law that when a quantity of heat H, falls by a reversible cyclical process through the temperature dT the maximum amount of work which it can produce is:

$$dW = H\frac{dT}{T}.$$

Substituting the above values in this formula gives:

$$jFdE = j(FE - Q)\frac{dT}{T}, \text{ or}$$

$$E = \frac{Q}{jF} + T\frac{dE}{dT}, \tag{2}$$

which is the Gibbs-Helmholtz equation. It is evident from this that the electromotive force of a cell can be calculated by the

formula $E = \frac{Q}{jF}$ from the heat of the reaction when the temperature

coefficient is zero. This was formerly supposed to be true in all cases and is known as *Thomson's rule*. In many cases it can be used where an accuracy better than 10 percent is not required.[1] If the temperature coefficient is positive, the cell takes up heat

[1] Thompson, J. Am. Ch. Soc. **28**, 731 (1906).

from the surroundings and delivers more electric energy than corresponds to the heat of the reaction, while if negative, less is delivered and the rest is given up to the surroundings. Table 14 contains data taken for the purpose of testing this equation.[1]

TABLE 14. THE GIBBS-HELMHOLTZ EQUATION

CELL	E IN VOLTS	$\frac{dE}{dT}$	Q IN CALORIES		
			Calc from E and $\frac{dE}{dT}$	By Calorimetric Measurement	By Thomson Rule = $\frac{\nu FE}{4 \cdot 19}$
Cu|Cu(C₂H₃O₂)₂ Pb(C₂H₃O₂)|Pb	0.4764 $t = 0°$	+ 0.000385	16900	17533	21684
Cu|CuSO₄ ZnSO₄|Zn sols. sat. at 15°	1.0934 $t = 15°$	− 0.000429	56089	55189	50395
Ag | AgCl ZnCl₂ + 100 H₂O|Zn	1.015 $t = 0°$	− 0.000402	51989	52046	46907
Hg|HgCl 0.01 NKCl|N KNO₃| 0.01 N KOH Hg₂O|Hg	0.1636 $t = 18.5$	+ 0.000837	− 3710	− 3280	7566

It will be noticed that the agreement of the values in columns 4 and 5 is better than that in 5 and 6, and that in the last cell even the sign of the heat effect calculated by Thomson's rule is wrong.

Heats of reaction can be calculated from potential measurements at two different temperatures by the Gibbs-Helmholtz equation; the reverse is evidently not possible. However, electromotive force values of certain *reversible* cells can be calculated by the third law of thermodynamics from purely thermal data, and values for *reversible concentration* cells can be calculated (1) by the following historically important osmotic theory of Nernst, or (2) by considering the change to take place in two different reversible ways, one of which is in a voltaic cell, and equating the corresponding two expressions for free energy. These methods will now be described.

Nernst's Osmotic Theory of Electromotive Force.[2] — The fundamental conception of this theory is that electromotively active substances have a tendency to go in solution as charged ions. This tendency is called the *electrolytic solution pressure* of the

[1] See Jahn, Wied. Ann. **50**, 189 (1893); Bugarsky, Z. anorg. Ch. **14**, 145 (1897); Cohen, Z. phys. Ch. **60**, 706 (1907).
[2] Z. phys. Ch. **4**, 129 (1889).

substance. It is constant for each substance at a given temperature and pressure and for a given solvent.

A metal dipping in pure water thus tends to dissolve as positively charged ions, leaving the metal negatively charged ; these ions are therefore attracted to the surface, forming what is known as a *double layer*. The attraction between the metal and the ions increases with the number of ions sent out, and finally becomes so great that no more ions can leave the metal. If the liquid in which the metal dips is a solution of a salt of this metal, the osmotic pressure of the ions already present also opposes the further formation of ions from the metal. If (1) the osmotic pressure p is equal to the electrolytic solution pressure P, no ions will go in solution and there will be no difference in potential. If $P > p$, ions will go in solution until the following equation is satisfied :

$$P = p + x,$$

where x is the electric attraction between the metal and the ions. If (3) $P < p$, then ions deposit on the metal until the osmotic pressure equals the electrolytic pressure plus the electrostatic repulsion between the positively charged metal and the positive ions in solution. Then,

$$P + x = p.$$

Similar relations hold if the electrode sends out negative ions, as in the case of the halogens.

The electromotive force between the liquid and the metal can be calculated as follows.

In Figure 20 suppose the cylinder contains a metal electrode at the bottom and a frictionless piston permeable to water but not to the ions sent off by the electrode. Suppose there is an infinitesimal film of solution of ions of the electrode between the piston and the electrode, with the osmotic pressure p. (1) Allow ν faradays of electricity to pass from the electrode to the solution, where ν is the valence of the ions, and allow the piston to rise so as to keep the pressure p constant. If **E** is the potential difference at the electrode, the work done by the machine is,

$$\mathbf{E}F + kpv,$$
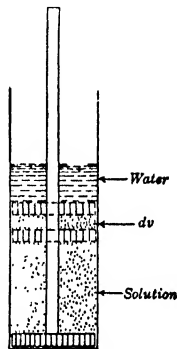
where v is the volume of solution containing one gram atom of the ions in question, and where k is the factor to change liter-atmospheres, in which R is supposed to be expressed, into joules, and equals $1000 \times 13.596 \times 76 \times 10^{-7} = 101.4$. (2) Allow the ions to expand to the volume $v + dv$, producing the work $kpdv$. The potential difference at the electrode is now $\mathbf{E} + d\mathbf{E}$. (3) Pass the same quantity of electricity in the reverse direction, and allow the piston to sink so as to keep the pressure constant. The piston will now be in the original position, and the only difference in the state of the system before and after the experiment is that the film of solution contains ions at the osmotic pressure $p + dp$, which would give a negligible amount of work in returning to the pressure p. The work done by the system in the last operation is therefore

$$- v(\mathbf{E} + d\mathbf{E})\mathbf{F}.$$

The sum of the quantities of work performed in these three steps must be zero, otherwise perpetual motion would be possible. That is,

$$- v\mathbf{F}d\mathbf{E} + kpdv = 0.$$

Integrating this gives,

$$v\mathbf{E}\mathbf{F} = - kRT \int \frac{dp}{p} + const.$$
$$= - kRT \ln p + const.$$

The constant can be put in the form $kRT\ln P$, and the equation then becomes,

$$\mathbf{E} = \frac{kRT}{v\mathbf{F}} \ln \frac{P}{p}. \tag{3}$$

This equation is a mathematical statement of the Nernst osmotic theory of electromotive force, and is of fundamental importance in electrochemistry. If $P = p$, the electromotive force is zero, so this integration constant may be considered the electrolytic solution pressure.

Substituting in the values of the constants, changing the natural logarithms to the base 10, and placing $T = 273° + 18°$, gives

$$\mathbf{E} = \frac{101.4 \times 0.0821 \times 291}{0.4343 \times 96500 \, v} \log \frac{P}{p} = \frac{0.05780}{v} \log \frac{P}{p}. \tag{4}$$

For 25° C. the numerical factor is 0.05916.

E is called the *electrode potential* of the electrode, and E^o is the value of E when the concentration of the ions that determine the electrode potential is *molal;* that is, one mol per 1000 g. of water.

It must be remembered that in this derivation the solution is supposed to obey the gas law.

If two electodes consisting of metals dipping in solutions of their salts are combined to form the cell,

$$M_1|M_1X|M_2X|M_2,$$

its electromotive force would be,

$$E = \frac{RT}{\nu_1 F} \log \frac{P_1}{p_1} - \frac{RT}{\nu_2 F} \log \frac{P_2}{p_2}, \tag{5}$$

neglecting the potential difference at the junction of the two liquids. Whether the two single values are to be added or subtracted depends on the case considered, for the electrodes may assist or oppose each other. (See also page 100.)

When the Nernst osmotic theory was first tested experimentally, it was found that the results were in approximate agreement with the theory, when the ion concentrations were calculated from conductance ratios. More careful work has shown, however, that, as in the case of the mass action law, activities and not conductance ratios should be used in these formulas. Up to concentrations of 1 molal, however, approximately correct results are calculated from conductance ratios, and in the following examples both conductance ratios and activities will be used, according to the example chosen.

According to the theory here presented practically the entire electromotive force of a galvanic cell is situated at the junctions of the two electrodes with the electrolyte. Recent work, however, on the electron emission from heated metals, photo-electric phenomena, and contact potentials has shown that a large part of the electromotive force of a cell is due to the contact potential between the two metals of the electrodes, and thus Volta's original theory, discredited among chemists since the work of Ostwald and Nernst (1889 to 1893) on the electromotive force of voltaic cells, has been found in the main to be correct. The values of electrode potentials include the potential differences of the metals, and this will be the best method until the absolute values of electrode potentials can be determined.[1]

---

[1] Langmuir, Tr. Am. Electroch. Soc. **29**, 125 (1916); Lewis and Randall, *Thermodynamics,* p. 401 (1923).

(1) The cell,

Zn amalgam C_1|ZnSO$_4$ sol.|Zn amalgam C_2,
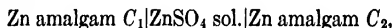
has the electromotive force,

$$\mathbf{E} = \frac{RT}{2\,\mathbf{F}} \log \frac{P_1}{p_1} - \frac{RT}{2\,\mathbf{F}} \log \frac{P_2}{p_2}. \tag{6}$$

The electrolytic solution pressure of zinc in amalgams may be considered proportional to its osmotic pressure in the amalgam, and this in turn is proportional to its concentration. Therefore this reduces to,

$$_4\mathbf{E} = \frac{RT}{2\,\mathbf{F}} \log \frac{C_2}{C_1}, \tag{7}$$

where the C's are the concentrations of zinc in the amalgams. Equation (7) for amalgams had been derived by several others before the publication of Nernst's theory.[1] Thus it can be derived by purely osmotic considerations, as follows: When the cell delivers energy, zinc dissolves from the more concentrated amalgam and deposits in the less concentrated. The maximum amount of work obtainable from the reversible expansion of one gram mol of any dissolved substance that obeys the gas law, from the concentration C_2 to C_1 is $RT \log \dfrac{C_2}{C_1}$. If this process delivers electric work in place of osmotic work, it will have the value $2\,\mathbf{EF}$, which must be equal to the osmotic work, as both processes are supposed to take place reversibly and isothermally and therefore give the maximum values of free energy. Equating these two quantities gives equation (7). This deduction assumes that the dissolved substance is monatomic, and that the gas law holds.

This equation has been tested by Richards between 0° C. and 40°, with the result that when the concentration is less than 0.01 gram atom per liter, the amalgams of thallium, indium, tin, zinc, lead, copper, and lithium behave as ideal solutions.[1] Deviations occur with higher concentrations. In the case of thallium solutions measured up to 45 percent solutions, the measured values are nearly twice as large as required by the formula at the higher concentrations, while with lead and tin they are lower.

[1] Richards and Wilson, Pub. Carnegie Inst. **118**, 3 (1909).

(2) Another important type of concentration cell is,

$$Ag|AgNO_3 \text{ sol. conc. } C_1|AgNO_3 \text{ sol. conc. } C_2|Ag,$$

for which

$$E = \frac{RT}{F}\log\frac{P}{p_1} - \frac{RT}{F}\log\frac{P}{p_2} = \frac{RT}{F}\log\frac{p_2}{p_1} = \frac{RT}{F}\log\frac{C_2\gamma_2}{C_1\gamma_1}. \quad (8)$$

γ_1 and γ_2 are the dissociations of the two solutions. Nernst measured this cell and found 0.055 volt, while the calculated value is 0.054.

The calculation of the electromotive force of this cell from osmotic work is as follows. When one faraday is taken from the cell, one equivalent of silver dissolves in the dilute solution and an equal amount deposits from the concentrated. At the same time ions move across the junction of the solutions. If n is the transference number of the nitrate ion in silver nitrate, $1 - n$ equivalent of silver migrates from the dilute to the concentrated solution, leaving n more equivalent in the dilute solution than at the start. Likewise n equivalent of nitrate ion has migrated from the concentrated to the dilute solution. The total osmotic work obtainable from this process is therefore,

$$2\,nRT\log\frac{C_2\gamma_2}{C_1\gamma_1} = EF. \quad (9)$$

This agrees with the Nernst equation (8) only when $n = \frac{1}{2}$. The reason for this difference is that in the Nernst derivation no account is taken of the difference of potential at the junction of the two liquids. The difference between these two values of E therefore must give the electromotive force at this junction:

$$E \text{ at liquid-liquid junction} = (1 - 2\,n)\,\frac{RT}{F}\log\frac{C_2\gamma_2}{C_1\gamma_1}. \quad (10)$$

If the metal is ν-valent, and dips in a solution of one of its salts which dissociates into m ions of anionic transference number n, the above derivation will give the result,

$$E = \frac{mnRT}{\nu F}\log\frac{C_2\gamma_2}{C_1\gamma_1}. \quad (11)$$

(3) The cell

$$Zn|ZnCl_2 \text{ sol. conc. } C_1|Hg_2Cl_2|Hg|Hg_2Cl_2|ZnCl_2 \text{ sol. conc. } C_2|Hg$$
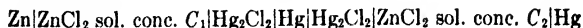
differs from the cell

$$Zn|ZnCl \text{ sol. conc. } C_1|ZnCl_2 \text{ conc. } C_2|Zn$$
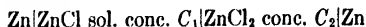
by having the mercury electrode inserted in the middle so that there is no possibility of zinc chloride migrating from one concentration to the other. These are called *concentration cells without transference*. When the cell is active, solid mercurous chloride disappears from one side and appears on the other, but this involves no mol. Also one mol of zinc ions is changed reversibly from the higher concentration $C_2\gamma_2$ to the lower concentration $C_1\gamma_1$, which is capable of furnishing the work,

$$RT \log \frac{C_2\gamma_2}{C_1\gamma_1},$$

while the two mols of chlorine ions that accompany the zinc if transferred reversibly from the higher to the lower concentration are capable of furnishing twice this amount of work. Placing the sum of these equal to the electric work and dividing by 2 **F** gives

$$\mathbf{E} = \frac{3}{2}\frac{RT}{\mathbf{F}} \log \frac{C_2\gamma_2}{C_1\gamma_1}. \tag{12}$$

It would make no difference if some other metal and one of its slightly soluble salts replaced mercury and calomel. This is shown in Table 15.[1]

TABLE 15. ELECTROMOTIVE FORCES OF CELLS OF THE TYPE
Zn|ZnCl₂ Hg₂Cl₂|Hg|Hg₂Cl₂ ZnCl₂|Zn and Zn|ZnCl₂ AgCl|Ag|AgCl ZnCl₂|Zn

CONC OF ZnCl₂	OBSERVED E.M.F OF CELLS WITH		CALC. E.M.F.
	Hg|Hg₂Cl₂	Ag|AgCl	
0.2 — 0.02	0.0787	0.0767	0.0797
0.1 — 0.01	0.0800	0.0780	0.0818
0.02 — 0.002	0.0843	0.0843	0.0844
0.01 — 0.001	0.0861	0.0847	0.0853

Comparing equations (11) and (12), it is evident that the transference number of zinc chloride can be determined by dividing one of these equations by the other.[2] In fact, this gives the most accurate method of obtaining transference numbers. Direct division is allowable only when the transference number is constant between the concentrations of the two solutions. When it changes,

[1] Goodwin, Z. phys. Ch. **13**, 577 (1894).
[2] See MacInnes and Parker, J. Am. Ch. Soc. **37**, 1457 (1915); MacInnes and Beattie, J. Am. Ch. Soc. **42**, 1117 (1920).

it is possible to calculate the values of transference numbers for given concentrations.

Table 16 gives transference numbers obtained in this way.

TABLE 16. TRANSFERENCE NUMBERS OF LITHIUM CHLORIDE

CONC C	E M F METHOD	BEST VALUE, HITTORF METHOD
0.01	0.334	0.332
0.1	0.311	0.328
1.0	0.286	0.313
3.0	0.261	———

(4) The cell

$$Ag|AgNO_3|KNO_3|KCl \, AgCl|Ag$$
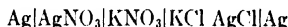
is similar to (2) above, in that it has two reversible electrodes of the same metal. The difference is that here the concentration of the silver ions at the right-hand electrode is very small. Electrodes of this kind, which are covered with an insoluble salt of the metal of the electrode, and which are in a solution of a salt containing the same anion as the insoluble salt, are called *unpolarizable electrodes of the second kind*, or *electrodes reversible with respect to the anion*. Formula (8) gives the electromotive force of this cell, when C_2 refers to the concentration of silver nitrate, C_1 to silver chloride. The concentration of silver ions in the potassium chloride solution can be found as follows. A saturated solution of silver chloride in pure water has been found by conductivity to be 0.0000144 normal. Since so dilute a solution is completely dissociated, each ion has this same concentration and the solubility product is

$$(Ag)(Cl) = 0.0000144^2 = S^2.$$

In the chloride solution the chloride ions from potassium chloride have the concentration C_3, and the chloride and silver ions from silver chloride the new value C_2. Since the solubility product is constant,
$$C_2(C_2 + C_3) = S^2$$

by equation 7, page 46, and since C_3 is relatively very large with respect to C_2,
$$C_2 = \frac{S^2}{C_3}.$$

If the potassium chloride is 0.1 normal, which is 85 percent dissociated, and the silver nitrate 0.1 normal and 82 percent dissociated, then

$$\mathbf{E} = \frac{RT}{\mathbf{F}} \log \frac{(0.082)(0.085)}{0.0000144^2} = 0.444 \text{ volt, while the experimentally}$$

determined value is 0.45.

Cells with Gas Electrodes. — Certain gases, such as hydrogen and chlorine, can be made to act as electrodes by bringing them in contact with platinized platinum dipping into a solution containing the ions of the gas. A cell of this kind can also be made by combining two electrodes with the hydrogen at different pressures, dipping into solutions of the same hydrogen ion concentration. If the electrolytic solution pressures in the two electrodes are P_2 and P_1, then by the Nernst formula,

$$\mathbf{E} = \frac{RT}{\mathbf{F}} \log \frac{P_2}{P_1},$$

since the osmotic pressures cancel. If one mol of hydrogen is allowed to expand reversibly from the gas pressure p_2 to p_1, it could do the work:

$$\frac{RT}{\mathbf{F}} \log \frac{p_2}{p_1}$$

and the same work electrically would be $2\,\mathbf{EF}$, since each molecule furnishes two ions. Therefore

$$\mathbf{E} = \frac{RT}{2\,\mathbf{F}} \log \frac{p_2}{p_1} = \frac{RT}{\mathbf{F}} \log \left(\frac{p_2}{p_1}\right)^{\frac{1}{2}},$$

and consequently for any diatomic gas giving two univalent ions the electrolytic solution pressures are proportional to the square root of the gas pressures.

Another concentration cell can be made having the gases of the two electrodes at the same pressure but dipping in solutions of different hydrogen ion concentration. An important case is when one solution is acid, the other alkaline. If both are 0.1 molal, then the activity of the hydrogen ions in the acid is 0.084 (Table 18), and from the measured voltage of the cell the concentration of hydrogen ions in the alkali can be calculated as follows. Taking into account the potential difference at the liquid-liquid junction, at 25° this cell has the voltage 0.7008.[1] Therefore

$$0.7008 = 0.05916 \log \frac{0.084}{C},$$

[1] Lorenz and Böhi, Z. phys. Ch. **66**, 733 (1909); Lewis and Randall, J. Am. Ch. Soc. **36**, 1969 (1914); *Thermodynamics*, p. 408 (1923).

from which the activity of hydrogen ions in the alkali solution is,

$$C = 0.084 \times 10^{-11\ 85}.$$

According to the mass action law,

$$\frac{(OH^-)(H^+)}{(H_2O)} = \text{constant} = k_w,$$

and taking the activity of water as unity,

$$(OH^-)(H^+) = k_w, \tag{13}$$

for all solutions of pure water. Substituting the activity of hydroxyl ions in the 0.1 molal solution, 0.081, (13) gives

$$0.081 \times 0.084 \times 10^{-11\ 85} = 0.957\ 10^{-14}.$$

Since in pure water the hydroxyl ion concentration equals the hydrogen ion concentration,

$$(OH^-)(H^+) = \sqrt{0.957\ 10^{-14}} = 0.98\ 10^{-7},$$

which agrees very well with the value $1.07\ 10^{-7}$ calculated from Kohlrausch's conductivity measurements at $25°$ C. (See page 44.) The following values calculated by Lewis and Randall by another method are doubtless the best values at present:

	$0°$	$18°$	$25°$
k_w	$0.114\ 10^{-14}$	$0.58\ 10^{-14}$	$1.005\ 10^{-14}$

At $100°$ $k_w = 48 \times 10^{-14}$.[1]

Activities of Ions. — Attention has been called to the fact both in the present chapter and in that on Conductivity that the activities of ions are not equal to their concentrations, except in very dilute solutions. Activities can be determined by freezing-point lowering, by the effect of salts on the solubility of one another, from vapor pressure, and from electromotive force values. Only the last two will be considered here.

When an electrolyte has a measurable vapor pressure, the activity of the electrolyte in the solution and in the gas phase must be equal because they are in equilibrium. Since the activity of a perfect gas is equal to its concentration, and since gases at low pressures are perfect, the ratio of the vapor pressures is equal to that of the activities.

Thus the partial vapor pressures of 10 and 7 formal hydro-

[1] Noyes, Carnegie Institution of Washington, publication No. **53**, p. 185 (1907).

chloric acid solutions at 25° C. are 4.2 and 0.14 mm. of mercury an⌐ the ratio of the activities of un-ionized HCl is therefore:

$$\frac{a_1}{a_2} = \frac{4.2}{0.14} = 30.$$

But by the mass action law $a_{HCl} = k(a_{H+})(a_{Cl-})$, therefore [1]

$$\frac{(p_{HCl})_1}{(p_{HCl})_2} = \frac{(a_{HCl})_1}{(a_{HCl})_2} = \frac{(a_{H+})_1(a_{Cl-})}{(a_{H+})_2(a_{Cl-})_2}. \tag{14}$$

The determination of electromotive force is of more general applicability than the method just given. The type of cell used for this purpose is:

$$H_2(1 \text{ atm.})HCl \ C_1 \text{ molal, } AgCl|Ag|AgCl, HCl \ C_2 \text{ molal } H_2 \ (1 \text{ atm.})$$

for which
$$E = \frac{2\,RT}{F} \log \frac{C_2\alpha_2}{C_1\alpha_1}, \tag{15}$$

derived by substituting (14) in

$$EF = RT \log \frac{(p_{HCl})_1}{(p_{HCl})_2},$$

where $C_1\alpha_1$ and $C_2\alpha_2$ are the square roots of the products of the activities of the two ions. If this cell is measured, α_2 can be calculated if C_2, C_1, and α_1 are known.

At low concentrations the activity of the ions is assumed equal to the concentration of the ion constituent. In this way the square roots of the product of activity coefficients of ions can be found.

Table 17 gives this activity coefficient for a number of the more important electrolytes.

The activity coefficients all go through minimum values, as shown by the curves in Figure 21, which gives the activity coefficients and conductance ratios for hydrochloric acid. One of the problems of the theory of solution is to account for differences between the activity coefficients and the conductance ratios. At present there is no known relation between them.

The absolute ion activities cannot yet be determined, but by assuming, as suggested by MacInnes, that at each concentration

the two ions of potassium chloride be considered to have the same activity on the grounds that they have the same weight and mobility, individual activity coefficients for ions have been cal-
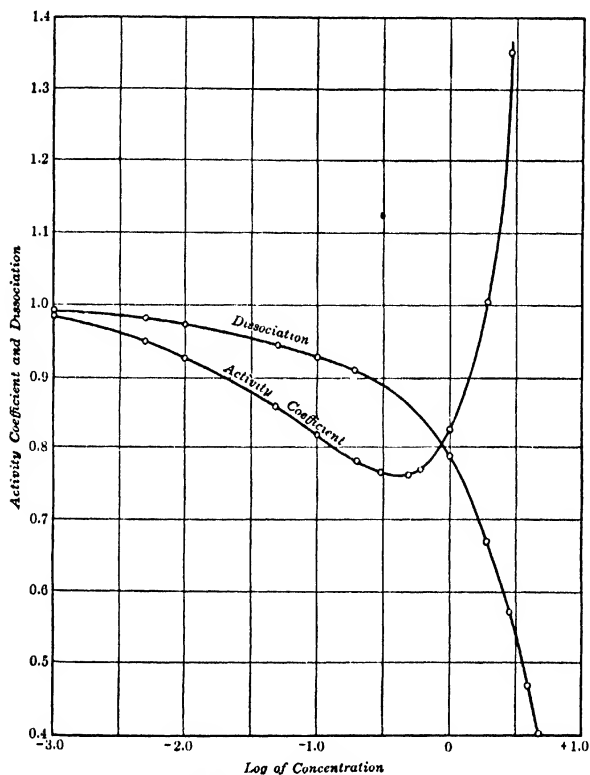
FIG. 21. — DISSOCIATION, AND ACTIVITY COEFFICIENT

culated by Lewis and Randall, as follows: From Table 17 α_{KCl} at 0.01 molality is 0.922 for each ion. Therefore for KIO_3

$$\alpha_{IO_3} = \frac{(.882)^2}{.922} = 0.845.$$

TABLE 17. ACTIVITY COEFFICIENTS OF TYPICAL ELECTROLYTES

Lewis and Randall, *Thermodynamics*, p. 362 (1923)

MOLALITY *	0 01	0.02	0 05	0 1	0.2	0.5	1	3
HCl (25°)	0.924	0.894	0.860	0.814	0.783	0.762	0.823	1.35
LiCl (25°)	0.922	0.892	0.843	0.804	0.774	0.754	0.776	1.20
NaCl (25°)	0.922	0.892	0.842	0.798	0.752	0.689	0.650	0.704
KCl (25°)	0.922	0.892	0.840	0.794	0.749	0.682	0.643	
KOH (25°)	0.92	0.89	0.84	0.80	0.75	0.73	0.75	
KNO_3	0.916	0.878	0.806	0.732				
$AgNO_3$	0.902	0.857	0.783	0.723	0.655	0.526	0.396	
KIO_3, $NaIO_3$	0.882	0.840	0.765	0.692				
$BaCl_2$	0.716	0.655	0.568	0.501				
$CdCl_2$ (25°)	0.532	0.44	0.30	0.219				
K_2SO_4	0.687	0.614	0.505	0.421				
H_2SO_4 (25°)	0.617	0.519	0.397	0.313	0.244	0.178	0.150	0.170
$La(NO_3)_3$	0.571	0.491	0.391	0.326	0.271			
$MgSO_4$	0.404	0.321	0.225	0.166	0.119			
$CdSO_4$	0.404	0.324	0.220	0.160				
$CuSO_4$	0.404	0.320	0.216	0.158	0.110	0.067		

* Molality is the number of mols per 1000 grams of water.

TABLE 18. ACTIVITY COEFFICIENTS OF INDIVIDUAL IONS AT
VARIOUS IONIC STRENGTHS

Lewis and Randall, *Thermodynamics*, p. 382 (1923)

MOLALITY	0 001	0 002	0 005	0 01	0.02	0.05	0.1
H^+	0.98	0.97	0.95	0.92	0.90	0.88	0.84
OH^-	0.98	0.97	0.95	0.92	0.89	0.85	0.81
Cl^-, Br^-, I^-	0.98	0.97	0.95	0.92	0.89	0.84	0.794
Li^+	0.98	0.97	0.95	0.92	0.89	0.85	0.81
Na^+	0.98	0.97	0.95	0.92	0.89	0.84	0.80
K^+, Rb^+, Cs^+	0.98	0.97	0.95	0.92	0.89	0.84	0.79
Ag^+	0.97	0.96	0.93	0.90	0.85	0.80	0.77
Tl^+	0.97	0.96	0.93	0.90	0.85	0.75	0.64
NO_3^-	0.97	0.96	0.94	0.91	0.87	0.77	0.68
ClO_3^-, BrO_3^-, IO_3^-	0.95	0.93	0.89	0.85	0 79	0.70	0.61
Me^{++}	0.78	0.74	0.66	0.60	0.53	0.43	0.34
SO_4^{--}	0.77	0.71	0.63	0.56	0.47	0.35	0.26
La^{+++}, $Fe(CN)_6^{---}$	0.73	0.66	0.55	0.47	0.37	0.28	0.21

In this way the figures given in Table 18 have been calculated. Under Me are included Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cu^{++}, Zn^{++}, Cd^{++}. For Cd the values are not to be used for obtaining the activity coefficients of halides.

Electromotive Forces Due to Mechanical Forces. — It is an interesting fact that mechanical forces can produce electromotive forces in voltaic cells. Thus an iron electrode under strain has a slightly different electromotive force than when unstrained. Above the elastic limit this amounts to several hundredths of a volt, below this limit the change in electromotive force is smaller.[1]

If two electrodes of the same metal are placed one above the other in the same solution, there will be a difference of potential between the two, because of the transfer of material from one electrode to the other when a current passes, as was shown must be the case by Maxwell in 1878. In a cell consisting of two zinc electrodes placed one above the other in a 1 percent zinc sulphate solution, the positive current flows from the lower to the upper electrode because while 32.5 grams of zinc move upward, 57.7 grams of sulfate ions move downward.[2]

This effect can be increased by using centrifugal force in place of gravity. Measurements of this kind have been made and found to agree with those calculated.[3]

Another cell depending on mechanical forces for its electromotive force is the following:[4]

Hg, pres. greater than 1 atm.|Hg_2^{++} solution|Hg, pres. 1 atm.

The electrode at high pressure was constructed by filling with mercury a tube h centimeters long, the lower end of which was closed with parchment and placed in the solution. When the cell is active, the mercury at the higher pressure goes into solution. When one faraday of electricity passes, 200 grams of mercury disappear from the top of the column and appear in the electrode at atmospheric pressure, which is placed at the level of the lower end of the tube. The mechanical work which 200 grams falling through a height h can do is $200\,h\ 9.807\ 10^{-5}$ joules, which must equal the electrical work **EF**. Table 19 shows the results of measurement and calculation.

[1] Walker and Dill, Tr. Am. Electroch. Soc. **11**, 153 (1907).
[2] Ramsey, Phys. Rev. **13**, 1 (1901).
[3] Tolman, Proc. Am. Acad. **46**, 109 (1911).
[4] Des Coudres, Wied. Ann. **46**, 292 (1892).

TABLE 19. E.M.F. OF THE CELL

Hg high pres.|Hg_2^{++} salt|Hg 1 atm.

λ IN CM.	E.M.F. CALC.	E.M.F. MEAS.
36	$7.2 \; 10^{-6}$	$7.4 \; 10^{-6}$
46	$9.3 \; 10^{-6}$	$10.5 \; 10^{-6}$
13	$23 \;\; 10^{-6}$	$21 \;\; 10^{-6}$

Potential Differences at Liquid-Liquid Junctions. — If one faraday of electricity is passed across the junction of two solutions of different concentrations of the same uni-univalent salt, from the higher to the lower concentration, $1 - n_a$ equivalent of cations moves from the higher to the lower concentration, and n_a equivalent of anions in the opposite direction. The work which the two could furnish if this were carried out by an osmotic reversible process is,

$$(1 - n_a)RT \log \frac{C_2 \alpha_2}{C_1 \alpha_1} - n_a RT \log \frac{C_2 \alpha_2}{C_1 \alpha_1} = \mathbf{E F},$$

or

$$\mathbf{E} = \frac{(1 - 2 \, n_a)}{\mathbf{F}} \, RT \, \log \frac{C_2 \alpha_2}{C_1 \alpha_1},$$

using activities in place of conductance ratios. With this difference this is equation (10). If its value $\dfrac{U_a}{U_a + U_c}$ is substituted for n_a, this reduces to the equation

$$\mathbf{E} = \frac{U_c - U_a}{U_c + U_a} RT \log \frac{C_2 \alpha_2}{C_1 \alpha_1}. \tag{16}$$

$\dfrac{\Lambda_c}{\Lambda_a + \Lambda_c}$ could also be substituted for n_a.

From this derivation it is evident that the potential difference in the liquid junction is due to differences in the migration velocities of the ions, or, what amounts to the same thing, to the different rates at which the ions tend to diffuse. In diffusing from a higher concentration to a lower, the more rapidly moving ion passes into the dilute solution in advance of the slower ion, and gives this solution its charge. This process is quickly retarded by this charge, which attracts the more slowly moving ion and repels the other, thus equalizing their diffusion.

If the ions have different valences, a similar calculation to the above gives in place of (16),

$$E = \frac{\dfrac{U_c}{\nu_c} - \dfrac{U_a}{\nu_a}}{U_c + U_a} \log \frac{C_2 \alpha_2}{C_1 \alpha_1}. \tag{17}$$

For two solutions of the same concentration of different uni-univalent salts, Planck derived the formula,

$$E = \frac{RT}{F} \log \frac{U_c' + U_a''}{U_a'' + U_c'}. \tag{18}$$

The calculation of the potential difference between any solutions of any number of univalent ions has also been carried out by Planck.[1]

This case can be omitted here, however, for such complicated junctions can usually be avoided by one of the following methods.[2] If the junction consists of solutions of two different concentrations of a heavy metal, in place of using pure water for dissolving the salt of the heavy metal, a solution containing a higher concentration of an alkali salt with the same anion as the heavy metal salt is used. Then the two adjoining solutions have only a slightly different total concentration, and the potential difference is reduced to a negligible value. Another method is to join the two solutions by a salt solution whose ions have nearly the same migration velocity, for example, saturated potassium chloride or saturated ammonium nitrate.

Potential differences at liquid junctions can be determined experimentally by measuring cells in which the potential differences at the electrodes cancel, as in the cell,

$$\text{Hg|Hg}_2\text{Cl}_2 \text{ solid, 0.1-}n\text{-KCl|0.1-}n\text{-NaCl, Hg}_2\text{Cl}_2 \text{ solid|Hg.}$$
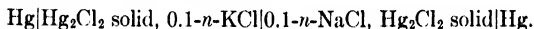
Another method is to measure two cells, in one of which the electrodes are reversible with respect to the cation, in the other with respect to the anion:[3]

$$\text{Zn|ZnSO}_4 \text{ sol. } C_1\text{|ZnSO}_4 \text{ sol. } C_2\text{|Zn,}$$
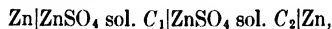
[1] Wied. Ann. **40**, 561 (1890). See also Henderson, Z. phys. Ch. **59**, 118 (1907).
[2] Bugarsky, Z. anorg. Ch. **14**, 150 (1897); Cumming, Tr. Faraday Soc. **2**, 213 (1906); **8**, 86 (1912); Cumming and Gilchrist, **9**, 174 (1913); Bjerrum, Z. phys. Ch. **53**, 428 (1905).
[3] Cohen and Tombrock, Z. Elektroch. **13**, 612 (1907).

for which
$$\mathbf{E}_1 = \frac{RT}{2\,\mathbf{F}} \log \frac{C_2\alpha_2}{C_1\alpha_1} + \mathbf{E}',$$

and $\text{Hg}|\text{Hg}_2\text{SO}_4,\ \text{ZnSO}_4\ \text{sol.}\ C_1|\text{ZnSO}_4\ \text{sol.}\ C_2,\ \text{Hg}_2\text{SO}_4|\text{Hg},$

for which $\mathbf{E}_2 = \dfrac{RT}{2\,\mathbf{F}} \log \dfrac{C_1\alpha_1}{C_2\alpha_2} + \mathbf{E}',$ from which $\mathbf{E}' = \dfrac{\mathbf{E}_1 + \mathbf{E}_2}{2}.$

Care is necessary in the manner in which the junction at two dissimilar solutions is made, if constant, reproducible values are desired. A method that has been used for this is to make the contact through a ground-glass stopper.[1] A better one is to bring the ends of the tubes containing the two liquids one directly above the other and then to surround this junction with a solution of concentration interme-

diate between the two, as in Figure 22. The denser liquid must be in the lower tube. This gives constant values for different concentrations of the same electrolyte.[2] Another
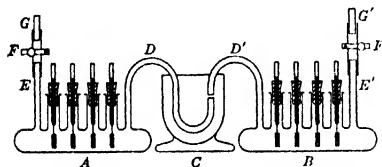
FIG. 22. — METHOD OF MAKING LIQUID-LIQUID JUNCTIONS OF CONSTANT E.M.F.

method consists in having the junction constantly renewed by a continuous flow of the two liquids.[3]

TABLE 20. POTENTIAL DIFFERENCES AT JUNCTIONS OF 0.1 N SOLUTIONS OF UNIVALENT CHLORIDES, AT 25°. THE DIRECTION OF E.M.F. IS LEFT TO RIGHT

ELECTROLYTES	E.M.F IN MILLIVOLTS	
	Measured	Calculated
HCl, KCl	26.78	28.4
HCl, NaCl	33.09	33.3
HCl, LiCl	34.86	35.8
HCl, NH₄Cl	28.40	28.6
KCl, NaCl	6.41	4.9
KCl, NH₄Cl	2.00	0.2

[1] Jones and Hartmann, J. Am. Ch. Soc. **37**, 752 (1915).

[2] MacInnes and Parker, J. Am. Ch. Soc. **37**, 1445 (1915); MacInnes and Beattie, *ibid*. **42**, 1117 (1920).

[3] Lamb and Larsen, J. Am. Ch. Soc. **42**, 229 (1920).

Table 20 contains observed differences of potential using a flowing junction, compared with results calculated by formula (18) slightly modified.[1]

The agreement is fairly good except where the potassium ion is involved.

Chemical Cells. — Concentration cells, such as those described above, have no chemical heat of reaction, except a small heat of dilution, and therefore the electricity which they deliver is derived from the heat of the surroundings. If the solutions obey the gas law, Q in the Gibbs-Helmholtz equation equals zero and this equation becomes $\mathbf{E} = T\dfrac{d\mathbf{E}}{dT}$, which integrated gives $\mathbf{E} = kT$; that is, the electromotive force is proportional to the absolute temperature. In chemical cells a chemical reaction takes place, which furnishes the greater part of the energy, and the quantity $T(d\mathbf{E}/dT)$ is of relatively small importance. Chemical cells have much larger electromotive forces than concentration cells, and are the only kind used to furnish electricity for technical purposes.

It is to be noticed that in chemical cells the substances that react on each other are never in direct contact. Thus the reaction furnishing the current in the Daniell cell is,

$$Zn + CuSO_4 = ZnSO_4 + Cu,$$
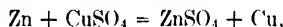
but zinc is not in contact with copper sulfate; if it were, no external current would be produced. For the production of an external current, the reacting substances must always be separated at the two electrodes by an intervening electrolyte. This has been called chemical action at a distance.[2]

Electromotive Force and the Third Law of Thermodynamics. — On account of the fact that thermal data are more numerous than free energy data, it has always seemed desirable to find a way of calculating free energies (and therefore electromotive forces) from thermal data. The third law of thermodynamics has finally made this possible. The thermal data required, however, are more extensive than those at present available, and include specific heats in the neighborhood of the absolute zero, so that this law has not made the determination of free energies any simpler than to measure them directly.

The following method of presentation is due to Nernst.[3] This law is

[1] MacInnes and Yeh, J. Am. Ch. Soc. **43**, 2563 (1921); Lewis and Sargent, J. Am. Ch. Soc. **31**, 363 (1909).

[2] Ostwald, Z. phys. Ch. **9**, 540 (1892).

[3] Nernst, *Theoretische Chemie*, 8–10 ed. (1921); *Grundlagen des Neuen Wärmesatzes* (1918); Coehn in Müller-Pouillets *Lehrbuch der Physik*, 10th ed. **4**, 559 (1909).

based on the observation that for a reaction between a number of *pure solid or liquid* substances, the difference between the free energy change and the total energy change is small. This led to the assumption that these two quantities are not only equal at the absolute zero, but that they approach each other asymptotically, as shown in Figure 23. In this case the following relation holds, using Nernst's notation:

$$\left(\frac{dA}{dT}\right)_{T=0} = \left(\frac{dU}{dT}\right)_{T=0}, \tag{19}$$

FIG. 23. — CHANGE OF ΔF AND ΔH WITH TEMPERATURE

where A is the free energy change and U the total energy change. It is also assumed that specific heats can be expressed with sufficient accuracy as a series of ascending powers of T in which the exponents are whole numbers. Consequently the heat of the reaction U is given by the formula,

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \cdots. \tag{20}$$

Substituting this in

$$A = U + T\frac{dA}{dT},$$

and integrating (with the help of the integrating factor $1/T^2$) gives

$$A = U_0 + aT - \alpha T \ln T - \beta T^2 - \tfrac{1}{2}\gamma T^3, \tag{21}$$

where a is an integration constant. Differentiating (20) and (21) gives,

$$\frac{dU}{dT} = \alpha + 2\beta T + 3\gamma T^2 + \cdots, \tag{22}$$

$$\frac{dA}{dT} = a - \alpha \ln T - \alpha - 2\beta T - \tfrac{3}{2}\gamma T^2. \tag{23}$$

In order that (19) shall hold it is necessary that both $a = 0$ and $\alpha = 0$, so that (20) and (21) become,

$$U = U_0 + \beta T^2 + \gamma T^3 + \cdots, \tag{24}$$

$$A = U_0 - \beta T^2 - \frac{\gamma}{2}T^3, \tag{25}$$

and free energy change is expressed in terms of thermal quantities only.

The values of β and γ are determined from the following relation between the temperature coefficient of the total energy change and the heat capacities of the substances before (C_1) and after (C_2) the reaction:

$$\frac{dU}{dT} = C_1 - C_2 = 2\beta T + 3\gamma T^2 + \cdots. \tag{26}$$

Though, according to Nernst, it is always possible to express specific heat as a series of integral powers of T, resulting in (20), still the more complicated

functions of Einstein or Debye are generally used. Two examples are given below of the use of the simple formulæ above; cases requiring the more complicated formulæ are beyond the scope of this book.

(1) This theorem can be applied to the cell,

$$Pb|sat. \; sol. \; PbI_2|I_2 \; solid + Pt,$$
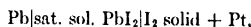
because saturated solutions are thermodynamically equivalent to solids. The reaction which furnishes the current is,

$$Pb + I_2 = PbI_2 + 41,850 \; cal.$$
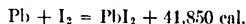
The difference between the heat capacities of the substances before and after the reaction at room temperature is $0.00061 \; T$, which by (26) equals $2 \, \beta T$, neglecting higher powers of T. Therefore $\beta = 0.00031$. Substituting this value of β and $T = 286$ in (24) gives $U_0 = 41,825$, and from (25)

$$2 \, EF = A = 41,825 - 0.00031 \times 286^2,$$

whence $E = \dfrac{41,800 \times 4.183}{2 \times 96,500} = 0.906$ volt as compared with 0.890 measured.

(2) In the cell,

$$Ag \; AgCl|sat. \; sol. \; PbCl_2|Pb,$$

the reaction is,

$$Pb + 2 \, AgCl = PbCl_2 + 2 \, Ag.$$
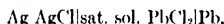
From thermochemical data,

$$U = 11,904 + 0.01006 \; T^2 + 0.0000171 \; T^3,$$

therefore,

$$A = 11,904 - 0.01006 \; T^2 - 0.00000855 \; T^3,$$

from which the electromotive force at $0°$ C. is calculated as 0.4915 while the measured value is 0.1912.

A more convenient method of applying the third law has been developed by G. N. Lewis and his collaborators.[1] Lewis states the third law as follows: "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, *every other substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.*"

Adopting Lewis' notation, the Gibbs-Helmholtz equation is expressed as follows:[2]

$$\Delta F = \Delta H - T \Delta S, \tag{27}$$

where ΔF is the increase in free energy, ΔH is the increase in total energy, and ΔS is the increase in entropy of the reaction. By comparing equation (27) with

$$\Delta F = \Delta H + T \frac{d \Delta F}{d T},$$

it is evident that $\Delta S = - \dfrac{d \Delta F}{d T}$.

[1] Lewis and Randall, *Thermodynamics*, p. 435 (1923).
[2] Lewis and Gibson, J. Am. Ch. Soc. **39**, 2554 (1917).

By means of the third law and by a knowledge of the specific heats at low temperatures, it is possible to calculate entropies at room temperature. Values of ΔF can then be found from equation (27) and from this, electromotive forces.

As an example take the reaction $Ag + \frac{1}{2}Hg_2Cl_2 = AgCl + Hg$, which can be made to take place reversibly in the cell:[1]

$$Ag|AgCl, KCl \text{ (molal) } \frac{1}{2}Hg_2Cl_2|Hg.$$
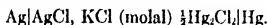
Here $\Delta H = 1275$ cal., and $\Delta S = 7.80$ cal./deg. calculated by the third law.

Whence by (27) $\Delta F = 1275 - 297.8 \times 7.80 = -1050$, and $E = \dfrac{1050 \times 4.18}{96,500}$

$= 0.0455$, which agrees with the measured value.

Another example is the cell:

$$Hg|Hg_2Cl_2, HCl(0.1 \text{ molal})|Cl_2,$$
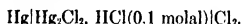
in which there action is $Hg + Cl = \frac{1}{2}Hg_2Cl_2$, for which $\Delta H = -31,300$ cal., $S_{298}HgCl = 23.2$, $S_{298}Hg = 17.8$, $S_{298}\frac{1}{2}Cl_2 = 26.3$. Therefore for this reaction, $\Delta S = 23.2 - (17.8 + 26.3) = -20.9$ cal. per degree, and therefore $\Delta F = -31,300 + 298 \times 20.9 = -25,073$ cal. Whence

$$E = \frac{25,073 \times 4.18}{96,500} = 1.086.$$

The measured value is 1.0896.[2]

It is beyond the scope of this work to go into the details of the calculation of entropies by the third law; all that can be done here is to point out that the third law makes this calculation possible, and from these entropies values of electromotive force may be computed.

Single Potential Differences and Their Algebraic Signs. —

The value of the electrolytic solution pressure is a characteristic quantity for each element and a table of these might be made, as of other natural constants. These would be of no use except to calculate electromotive forces, however, so in place of the electrolytic solution pressure a quantity is calculated known as the *normal potential*, the *electrolytic potential*, or the *molal electrode potential*. This is the potential difference between an electrode and a solution in which all substances taking part in the reaction are perfect solutes at the concentration of one mol per liter (*i.e.* the activity is molal), or, if gaseous, are perfect gases at one atmosphere.
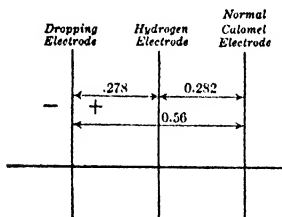
FIG. 24. — THE RELATION BETWEEN THE DROPPING, THE HYDROGEN, AND THE NORMAL CALOMEL ELECTRODES

[1] Gerke, J. Am. Ch. Soc. **44**, 1703 (1922).

[2] Lewis and Gibson, *l.c.*, p. 2577.

Table 21 gives the values of the more important molal potentials referred to the molal hydrogen electrode as zero. A cell made from a molal hydrogen electrode and a normal calomel electrode has a voltage of 0.2822 volt, the calomel electrode being the positive pole. Therefore if these values are to be referred to the normal calomel electrode as + 0.560, 0.278 must be added. Figure 24 represents the relation.

TABLE 21. MOLAL ELECTRODE POTENTIALS AT 25° C., REFERRED TO HYDROGEN AS ZERO. THE SIGN IS THAT OF THE CHARGE ON THE ELECTRODE

Lewis and Randall, *Thermodynamics*, p. 433 (1923).

Li, Li$^+$	− 2.9578	Fe, Fe^{+++}	− 0.045
Rb, Rb$^+$	− 2.9294	Pt, H$_2$, H$^+$	0
K, K$^+$	− 2.9224	Cu, Cu^{++}	+ 0.3448
Na, Na$^+$	− 2.7125	Hg, Hg$_2^{++}$	+ 0.7986
Zn, Zn^{++}	− 0.7581	Ag, Ag$^+$	+ 0.7995
Fe, Fe^{++}	− 0.441	Pt, S^{--} (rhomb.)	− 0.51
Cd, Cd^{++}	− 0.3976	Pt, OH$^-$, O$_2$	+ 0.3976
Tl, Tl$^+$	− 0.3363	Pt, I$^-$, I$_2$ (solid)	+ 0.5357
Sn, Sn^{++}	− 0.136	Pt, Br$^-$, Br$_2$ (liq.)	+ 1.0659
Pb, Pb^{++}	− 0.122	Pt, Cl$^-$, Cl$_2$ (gas)	+ 1.3594

The following are from LeBlanc, *Lehrbuch der Elektrochemie*, p. 263 (1922).

Ba, Ba^{++}	− 2.8	Sb, Sb^{+++}	+ 0.1
Sr, Sr^{++}	− 2.7	Bi, Bi^{+++}	+ 0.2
Ca, Ca^{++}	− 2.5	As, As^{+++}	+ 0.3
Mg, Mg^{++}	− 1.55	Cu, Cu$^+$	+ 0.52
Mn, Mn^{++}	− 1.0	Hg, Hg$^+$	+ 0.86
Cr, Cr^{++}	− 0.6	Au, Au^{+++}	+ 1.3
Cr, Cr^{+++}	− 0.5	Au, Au$^+$	+ 1.5
Co, Co^{++}	− 0.29	Pt, F$^-$, F$_2$ (gas)	+ 1.9
Co, Co^{+++}	+ 0.4		
Ni, Ni^{++}	− 0.22		

The following values of the electrode potentials involving the manganese ion in its different states of oxidation have been determined by Grube and Huberich.[1] These values are reduced by 0.004 volt on account of their use of 0.286 in place of 0.282 volt as the difference between the hydrogen and the normal electrodes.

POTENTIAL FORMING IONS IN RATIO 1:1	TOTAL METAL PER LITER IN GRAMS	H$^+$ CONC	TEMP DEGREES C.	POTENTIAL REFERRED TO THE H-ELECTRODE
Mn^{++},Mn^{3+}	2.75	15-n-H$_2$SO$_4$	12	+ 1.507
Mn^{3+},Mn^{4+}	2.75	15-n-H$_2$SO$_4$	12	+ 1.638
Mn^{++},Mn^{4+}	2.75	15-n-H$_2$SO$_4$	12	+ 1.573

[1] Z. Elektroch. **29**, 17 (1923).

The following are mostly from Foerster, *Elektrochemie wässeriger Lösungen*, p. 217 (1922).

POTENTIAL FORMING IONS IN RATIO 1 : 1	TOTAL METAL PER LITER	H + OR OH− CONC.	POTENITAL REFERRED TO THE H-ELECTRODE
$Sn_{,}^{++} Sn^{4+}$	0.36 Sn	0.6-n-NaOH	− 0.854
	0.50 Sn	1-n-HCl	+ 0.131
	0.50 Sn	0.5-n-HCl	+ 0.158
	0.50 Sn	2-n-HCl	+ 0.138
Cr^{++}, Cr^{+++}	1.7 to 2.4 Cr	0.1-n-HCl	− 0.400[1]
V^{++}, V^{+++}	0.1 V	1-n-H$_2$SO$_4$	− 0.204
Ti^{3+}, Ti^{4+}	0.45 Ti	4-n-H$_2$SO$_4$	+ 0.056
$Fe(CN)_6{}^{4-}, Fe(CN)_6{}^{3+}$	0.03 Fe		+ 0.406
Fe^{++}, Fe^{+++}	0.1 Fe as sulfate	{ weakly	+ 0.663
	0.1 Fe as chloride	{ acid	+ 0.714
Tl^+, Tl^{+++}	0.05 to 0.01-n Tl as sulfate	1.96 to 0.1-n-H$_2$SO$_4$	+ 1.2113
Ce^{3+}, Ce^{4+}	0.066 Ce	50 percent K$_2$CO$_3$	+ 0.063
Co^{++}, Co^{+++}	0.2 Co	2-n-H$_2$SO$_4$	+ 1.76

[1] Forbes and Richter, J Am Ch Soc **39**, 1140 (1917)

The following are from the J. Am. Ch. Soc. **45**, 377 (1923) by Smith and Swift.

$$Bi | BiO^+ + H^+, + 0.318 \text{ to } + 0.314.$$
$$Bi | Bi(OH)^{++} + H^+, + 0.310 \text{ to } + 0.298.$$
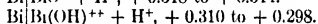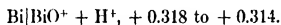
The relation between **E** and **E°** is as follows :

Equation (3) can be written,

$$\mathbf{E} = \frac{RT}{\nu\mathbf{F}} \log \frac{P}{p} = \frac{RT}{\nu\mathbf{F}} \log \frac{P}{kC} = \frac{RT}{\nu\mathbf{F}} \log \frac{P}{k} - \frac{RT}{\nu\mathbf{F}} \log C$$

$$= \mathbf{E°} - \frac{RT}{\mathbf{F}} \log C, \qquad (28)$$

where **E°** is the molal potential, k is a constant, and C is the ion concentration, or the activity, if the solute is not perfect.

It is necessary to indicate also the direction of potential differences at electrodes. This is done by prefixing a positive or a negative sign. Equation (28) gives the correct sign if this indicates the sign of the charge on the solution surrounding the electrode, and this convention is often used. It has the disadvantage that in a voltaic cell the more positive electrode is the *negative* pole. Therefore the reverse will be used here ; that is, the sign is that of

the charge on the electrode, and to meet this convention (28) must be written,

$$\mathbf{E} = \mathbf{E}° + \frac{RT}{\mathbf{F}} \log C. \qquad (29)$$

Thus for copper in molal cupric ions, $\mathbf{E}° = +\ 0.345$, and if $C > 1$, (29) shows $\mathbf{E} > \mathbf{E}°$, which is correct. For zinc, $\mathbf{E}° = -\ 0.758$, and the equation shows that if $C > 1$, $\mathbf{E}$ is numerically less than $\mathbf{E}°$, as it is in fact. According to this notation, a *more positive* potential means one *more noble*, or more like gold.

Electrodes Involving More Than One Ion. — Where the electrode reaction involves only one kind of ion, the formula connecting potential difference and ion-concentration is easily deduced from the Nernst equation as just shown, but for more complicated electrode reactions the general method of finding the expression for the free energy decrease of the reaction is necessary. The free energy content F of a system is so defined that its relation to the work content W is given by the equation,

$$F = W + pv.$$

Therefore in passing from the state 1 to the state 2 the decrease in free energy is,[1]

$$-\Delta F = F_1 - F_2 = W_1 - W_2 - (p_2v_2 - p_1v_1)$$
$$= W_1 - W_2 - \Delta(pv).$$

The decrease of free energy of a reaction is found as follows. Suppose a reaction takes place between a mols of A, b mols of B, etc., at concentrations C_A, C_B, etc., to form e mols of E, f mols of F, etc., at the concentrations C_E, C_F, etc., mols per liter. These are supposed to be in solution and all perfect solutes. The reaction is represented by the equation,

$$aA + bB + \dots = eE + fF + \dots.$$
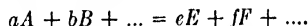
In order to have it furnish the maximum amount of work, which is the free energy decrease, the reaction must take place isothermally and reversibly. This can be done as follows. Let M in Figure 25 represent a chamber containing the substances in solution at the equilibrium concentrations represented by (A), (B), etc. The initial concentrations of the substances which disappear and the final concentrations of those which appear are represented by C's

[1] Noyes and Sherrill, *Chemical Principles*, p. 227 (1922); Lewis, J. Am. Ch. Soc. **35**, 14 (1913).

with subscripts. Connected to this chamber are as many cylinders as there are substances in the reaction, and each cylinder has a
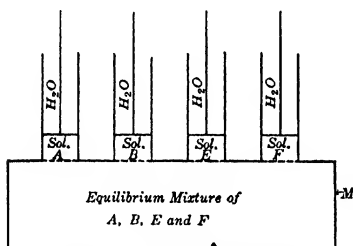
FIG. 25. — REACTION CHAMBER

frictionless piston which is semipermeable to the solvent but not to the solute. The cylinders can be separated from the reaction chamber by an impervious partition or by a membrane permeable only to the solute of the cylinder in question. Now start with a mols of A, b mols of B, etc., in their respective cylinders, with the impervious partitions in place, and allow the concentrations to change reversibly by the proper motion of the pistons to the equilibrium concentrations. The work done by a mols of A is

$$aRT \log \frac{C_A}{(A)} = RT \log \frac{C_A^a}{(A^a)},$$

and similar expressions for the other substances on the left. Now replace the impervious by the semipermeable membrane and force these substances into the reaction chamber. This involves no work. At the same time the substances on the left of the equation are forced in the chamber, those on the right are withdrawn so the concentrations in the chamber are not changed. Then in the cylinders containing the products of the reaction the semipermeable membranes are replaced by impervious walls and the concentrations are allowed to change reversibly from equilibrium to final concentrations. The work done by e mols of E is,

$$RT \log \frac{(E^e)}{C_E^e},$$

and similar expressions apply to the other products. The total work done by the reaction is therefore,

$$-\Delta F = RT\left(\log \frac{(E^e)(F^f) \dots}{(A^a)(B^b) \dots} - \log \frac{C_E^e \, C_F^f \dots}{C_A^a \, C_B^b \dots}\right)$$

$$= RT\left(\log K - \log \frac{C_E^e \, C_F^f \dots}{C_A^a \, C_B^b \dots}\right), \qquad (30)$$

where K is the equilibrium constant. If the initial and final concentrations are 1, then,

$$- \Delta F = RT \log K. \tag{31}$$

Exactly the same equations apply to gases, for which partial pressures are generally used in place of activities or concentrations.

If the reaction takes place in a cell, then $- \Delta F = \nu EF$, and equation (30) becomes,

$$E = \frac{RT}{\nu F}\left(\log K - \log \frac{C_E^e C_F^f \dots}{C_A^a C_B^b \dots}\right), \tag{32}$$

or if the initial and final concentrations are all 1,

$$E = \frac{RT}{\nu F} \log K. \tag{33}$$

Equation (30) also applies to the *electrode* reaction,

$$aA + bB + \dots + \nu F = eE + fF \dots. \tag{34}$$

By definition $E = E°$ when $C_A = C_B \dots = C_E = C_F \dots = 1$.

Therefore

$$E = E° - \frac{RT}{\nu F} \log \frac{C_E^e C_F^f \dots}{C_A^a C_B^b \dots}. \tag{35}$$

To meet the requirement of the arbitrary convention adopted regarding signs, this must be changed to read,

$$E = E° + \frac{RT}{\nu F} \log \frac{C_E^e C_F^f \dots}{C_A^a C_B^b \dots}, \tag{36}$$

which applies to any electrode potential, if the equation is written according to (34).

Thus for the hydrogen electrode,

$$H_2 + 2F = 2H^+,$$

and

$$E = E° + \frac{RT}{F} \log C_{H^+} - \frac{RT}{2F} \log p_{H_2}, \tag{37}$$

where p_{H_2} is the pressure of hydrogen gas in atmospheres.

It has been found that the electrode potentials of the hydrogen electrode agrees with the calculated values within the experimental error up to 100 atmospheres, and with slight deviations up to 400 atmospheres.[1]

[1] Hainsworth and MacInnes, J. Am. Ch. Soc. **44**, 1021 (1922).

For chlorine,

$$2 \, Cl^- + 2 \, F = Cl_2,$$
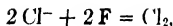
therefore,

$$E = E^\circ - \frac{RT}{F} \log C_{Cl^-} + \frac{RT}{2 \, F} \log p_{Cl_2}, \tag{38}$$

and for the lead peroxide electrode,

$$PbO_2^{--} + 2 \, F = PbO_2 \text{ solid,}$$
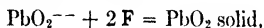
$$E = E^\circ - \frac{RT}{2 \, F} \log C_{PbO_2^{--}}. \tag{39}$$

The electrodes made from chlorine and hydrogen are reversible. Oxygen, however, does not give as high a voltage as it should. (See page 104.) Its value is also sensitive to light and to X-rays. The violet end of the spectrum lowers its electrode potential, while infra-red radiations raise it; that is, makes the hydrogen-oxygen cell have a higher electromotive force.[1]

The reaction taking place at the oxygen electrode may be either or both of the reactions,

$$2 \, O^{--} + 4 \, F = O_2 \text{ or } 4 \, OH^- + 4 \, F = 2 \, H_2O + O_2. \tag{40}$$
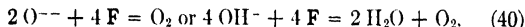
If the equilibrium reaction between O^{--} and OH^-,

$$2 \, O^{--} + 2 \, H_2O = 4 \, OH^-, \tag{41}$$
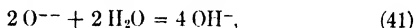
takes place instantly, it makes no difference which one is used. Since the activities are known for OH^- ions but not for O^{--}, it is more convenient to use the second reaction. The formula for the oxygen electrode potential would then be,

$$E = E^\circ - \frac{RT}{F} \log C_{OH^-} + \frac{RT}{4 \, F} \log p_{O_2}. \tag{42}$$

A different type of electrode are those in which an ion changes its state of oxidation. For example, when platinum dips in a solution of cupric and cuprous ions, the current causes the ions to change from one state to the other:

$$Cu^+ + F = Cu^{++},$$

or for iron,

$$Fe^{++} + F = Fe^{+++}.$$

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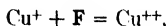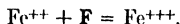
[1] Bose, Z. Elek. **7**, 672 (1901); Kochan, *ibid.* **9**, 33, 61, 79 (1903).

Substituting in (36), the following equation holds for copper,

$$E_{Cu} = E_{Cu}^{\circ} + \frac{RT}{F} \log \frac{C_{Cu^{++}}}{C_{Cu^{+}}},$$

and a similar one for iron.

The relation between the molal electrode potentials of,

(1) $\qquad$ E_1° for $Cu + 1\,F = Cu^+$,

(2) $\qquad$ E_2° for $Cu + 2\,F = Cu^{++}$,

(3) $\qquad$ E_3° for $Cu^+ + F = Cu^{++}$,

can be found by noticing that if the following cells are constructed,

$$Cu|Cu^{++} \; molal|Cu^+ \; molal|Cu,$$

$$Pt\left|\begin{matrix}Cu^+\\Cu^{++}\end{matrix}\right. \; molal|Cu^{++} \; molal|Cu,$$
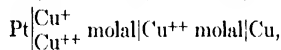
the reaction in both is the same: $2\,Cu^+ = Cu^{++} + Cu$, with the passage of $1\,F$ in each case, as can be shown by adding the reactions that take place at the electrodes when the current passes. Since the same reaction takes place in each cell, at the same concentrations, the free energy decreases must be equal; therefore,

$$F(E_1^{\circ} - E_2^{\circ}) = F(E_2^{\circ} - E_3^{\circ}),$$

which gives,[1]

$$E_2^{\circ} = \frac{E_1^{\circ} + E^{\circ}}{2}.$$

The general solution can be found from the fact that if the metal is oxidized directly to the high valence, whose value is denoted by h, the free-energy change must be the same as if it is first oxidized to the low valence, l, and then from this to the high. That is,

$$E_2^{\circ}hF = E_1^{\circ}lF + (h - l)E_3^{\circ}F,$$

whence

$$E_2^{\circ} = \frac{lE_1^{\circ} + (h - l)E_3^{\circ}}{h}. \tag{43}$$

The general expression for the electrode potential of this kind of electrode is,

$$E_3 = E_3^{\circ} + \frac{RT}{(h - l)F} \log \frac{(M^{h+})}{(M^{l+})}, \tag{44}$$

which is a special case of equation (36).

It is to be noticed that the molal electrode potential corresponding to oxidation from the lowest to the highest state always lies between those corresponding to oxidation from the lowest to the middle

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[1] Luther, Z. phys. Ch. **34**, 488 (1900); **36**, 385 (1901).

state and from the middle to the highest. The order, however, cannot be predicted. In the case of iron, reference to the table of molal potentials shows these potentials to be increasingly positive in the order E_1°, E_2°, E_3°, while for copper they are more positive .in the order E_3°, E_2°, E_1°.

A reaction such as,

$$Cr^{3+} + 4 H_2O + 3 F = CrO_4^{--} + 8 H^+$$
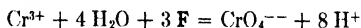
belongs to this same class, for the reaction is essentially

$$Cr^{3+} + 3 F = Cr^{6+},$$
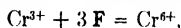
but its potential cannot be expressed in terms of Cr^{6+} because the concentration of these ions is not known. It would therefore be written,

$$E = E^\circ + \frac{RT}{3\,F} \log \frac{C_{CrO_4^-} \cdot C_{H^+}^8}{C_{Cr^{+++}}}. \tag{45}$$

The potential corresponding to this reaction, and of other similar ones is difficult to measure because of the slowness with which equilibrium at the electrode is reached. In some cases such potentials can be measured by adding small amounts of some unpolarizable substance which exists in two states of oxidation, such as ferrous and ferric ions. The reaction to be measured causes these to take in the solution a concentration ratio which gives the same potential as the reaction, and as these substances readily come to equilibrium with the electrode, they make the measurement of such potentials possible. Such substances may be called " potential catalyzers." [1]

Methods of Determining Absolute Electrode Potentials. — Since electrode potential differences can be measured only in pairs, in order to deduce values for single electrodes it is evidently necessary (1) to have at least one electrode for which the electrode potential is known, or (2) to assume some value arbitrarily for one electrode and refer all others to this. As a zero electrode potential has no theoretical significance, such as the absolute zero on the temperature scale has, it is of no great importance which is done.

There are three methods of constructing electrodes with electrode potentials theoretically equal to zero, but since they do not agree among themselves, they are no longer much used as standards, but the molal hydrogen electrode is arbitrarily placed equal to zero.

· These three methods of making electrodes with zero electrode potentials consist in (1) charging a mercury surface in contact

[1] Luther, Z. Elektroch. **13**, 289 (1907).

with dilute sulfuric acid until the surface tension is a maximum, (2) in allowing a stream of mercury to flow into a solution containing very few mercury ions, until the potential difference between the mercury and the solution is zero, and (3) by observing the motion of a particle of metal suspended in a solution of ions of the metal when a current passes through the solution. If the particle is positively charged, the positive charge will be attracted to the cathode and the negative charge on the double layer of the liquid will tend to move in the opposite direction. A motion of the particle toward the cathode should therefore result. If the polarity of the double layer is reversed, the motion should be reversed also. If there is no difference in potential, there is no charge and there should be no motion.[*] The concentration of the ions of the metal is therefore changed until the *isoelectric point*, at which there is no potential difference, is reached, as shown by the absence of motion, and it is then assumed that in this solution the electrode potential of the metal in question is zero.

(1) The surface-tension method depends on the work of Lippmann,[1] who found that the surface tension of a surface of mercury in contact with dilute sulfuric acid is a continuous function of the electromotive force of polarization on the same surface. The way this fact is used to determine single potentials is the following. A tube filled with mercury ending in a fine capillary dips in a solution with a very small mercury ion concentration, say potassium chloride saturated with mercurous chloride. At the bottom of the dish holding the solution is a layer of mercury. The surface tension of the mercury in the capillary
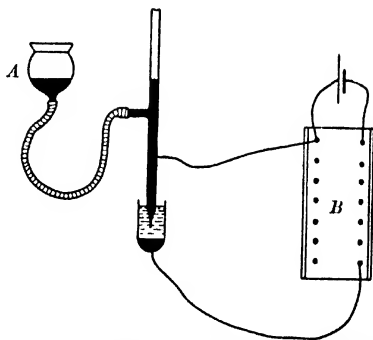
FIG. 26. — LIPPMANN CAPILLARY ELECTROMETER

prevents it from running out. By raising the bulb *A* in Figure 26 the pressure is increased until a little mercury is forced out of the capillary ; the bulb is then lowered so that the mercury rises and draws the solution in the capillary. The difference in poten-

[1] Pogg. Ann. **149**, 546 (1873).

tial between each mercury surface and the solution is the same; both are positively charged. This charge on the mercury as well as that on the solution repels itself and opposes the surface tension. Suppose now that a small electromotive force is applied in the direction to deposit mercury ions on the mercury in the capillary. This will dilute the solution around the mercury surface, and there will be a smaller charge on the mercury surface to keep the balance with the smaller osmotic pressure of the remaining mercury ions; that is, the potential difference between the mercury and the solution will be less. A smaller charge means an increase in the surface tension, since the charge repels itself and therefore counteracts surface tension, and the height of the mercury column will have to be increased to keep the meniscus in the capillary at the same position, which is observed in a small telescope. It is found that the height of the mercury column necessary to keep the meniscus in its position increases with the applied electromotive force to a maximum and then decreases. This maximum surface tension evidently corresponds to zero difference in potential at the mercury surface in the capillary. Now the important point is that the potential difference at the lower electrode is not changed by the applied electromotive force, because the current is too small to change the con-

FIG. 27. — THE RELATION BETWEEN POTENTIAL AND SURFACE TENSION OF A MERCURY SURFACE

centration of mercury ions when distributed over such a large surface. Therefore at the maximum surface tension the applied electromotive force is equal and opposite to the potential difference at

the lower electrode, and is therefore equal to the potential differ-
ence which a mercury surface assumes in the solution used.

Figure 27 shows the results obtained with normal hydrochloric
acid saturated with calomel.[1] The average maximum of the
curves comes at $+ 0.560$ volt, and the same would be found
with normal potassium chloride. Therefore by combining the
normal calomel electrode, $Hg|Hg_2Cl_2$, n-KCl, with any other elec-
trode and measuring the resulting cell, the other electrode po-
tential can be found.

(2) The dropping-electrode method of determining single
electrode potential differences depends on the fact first stated by
Helmholtz, that an insulated mass of mercury dropping into an
electrolyte can have no difference of potential with the electrolyte.
This is explained as follows. If mercury streams from a small
point into a solution of potassium chloride saturated with mercu-
rous chloride, as shown in
Figure 28, at first each drop
has mercury ions deposited
on its surface, giving it a
positive charge, surrounded
with an equal negative
charge in the solution.
When the drop reaches the
lower layer of mercury, it
gives its charge to this
layer, which gets rid of it
by sending mercury ions
into solution. These react
with the chlorine ions car-
ried down and form solid
mercury chloride. The so-
lution around the dropping
electrode will thus become
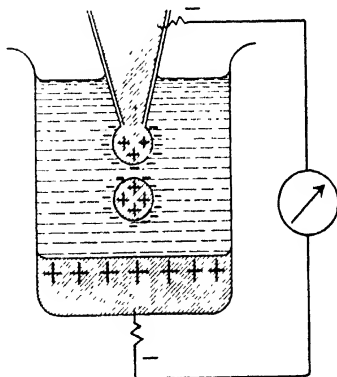
FIG. 28. — THE DROPPING ELECTRODE

more and more dilute until the concentration is reached at
which mercury ions are not deposited on the drops, and then the
potential difference is zero. Therefore the electromotive force
of the cell consisting of the dropping electrode and the lower
electrode gives the potential difference at the lower electrode.
In this way the normal calomel electrode was found to have a
potential difference of 0.56 volt.[2]

[1] Rothmund, Z. phys. Ch. **15**, 1 (1894).
[2] Paschen, Wied. Ann. **41**, 42 and 86 (1891); **43**, 568 (1891).

Diffusion causes difficulty in carrying out these measurements. This can be avoided if a solution is used which has just the concentration of mercury ions which gives zero difference of potential. By adding potassium cyanide the mercury ions can be made so dilute that the direction of the electric current between the two electrodes is reversed, and a concentration can be found at which there is no current. Therefore if a cell is made with mercury in contact with this zero solution for one electrode and the normal calomel electrode the other, the electromotive force of the cell is the potential difference at the calomel electrode. In this way the value for the tenth-normal electrode $Hg|Hg_2Cl_2$, 0.1-n-KCl was found to be 0.572,[1] while the surface-tension method gives 0.616. According to W. C. McC. Lewis[2] the dropping-electrode method is not accurate because the concentration change is said not to be due entirely to the relative values of osmotic and electrolytic solution pressures, but more largely to adsorption by capillarity.

(3) The third method was first used by Billiter (formerly Billitzer).[3] He used three modifications of the method: (a) the deflection of a minute ball fused at the end of a fine wire and suspended in the electrolyte by a quartz fiber was noted; (b) the direction of migration of colloidal metallic suspensions was noted; and (c) the potential difference at the ends of a tube of the electrolyte when a metallic suspension is allowed to fall through the electrolyte was noted. Billiter got consistent results by all three methods, — 0.125 volt for the 0.1-n calomel electrode, which is 0.7 volt different from that given by the first two methods. This work was repeated as nearly according to the directions given by Billiter as was possible by Goodwin and Sosman[4] without confirmation of methods a and b and by Whitney and Blake[5] without confirming method c. The same principle somewhat changed in detail has been used again recently by Garrison,[6] who finds Billiter's results confirmed; that is, he finds the absolute potential of the 0.1-n calomel electrode lies between $- 0.1$ and $- 0.02$ volt. Further work will evidently be necessary to settle this point.

Standard Electrodes. — The most commonly used standard electrode is the normal calomel electrode, $Hg|Hg_2Cl_2$, n-KCl sol.

[1] Palmaer, Z. Elektroch. 9, 754 (1903).
[2] Z. phys. Ch. 73, 146 (1910).
[3] Z. phys. Ch. 48, 513 (1904); 51, 166 (1905); Ann. der Phys. 11, 902, 927 (1903), Z. Elektroch. 8, 638 (1902).
[4] Tr. Am. Electroch. Soc. 7, 83 (1905).
[5] J. Am. Ch. Soc. 26, 1378 (1904).
[6] J. Am. Ch. Soc. 45, 37 (1923).

Its potential difference is taken either as $+ 0.560$ absolute or as $+ 0.2822$ referred to the molal hydrogen electrode as zero.[1]

The molal hydrogen electrode, consisting of hydrogen at atmospheric pressure against a solution of hydrogen at unit activity, is taken as zero at all temperatures. This is not identical with the hydrogen electrode adopted by Abegg, Auerbach, and Luther[2] in their bibliography of electromotive force data. They use a solution containing one gram atom of hydrogen ion per liter as determined by the conductance ratio, but unit hydrogen ion concentrations so determined have different activities for different acids. Thus the standard so defined gives potential differing by 0.03 volt when hydrochloric and sulfuric acids are used.

The following are some standard reference electrodes, at 25° C. referred to the molal hydrogen electrode.

From the electromotive force of the cell,[3]

$$H_2|HCl\ 0.1\ M,\ Hg_2Cl_2|Hg = 0.3989 \pm 0.0001\ volt\ = E_1,$$
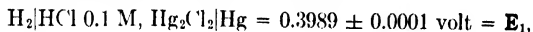
the tenth-normal calomel electrode, $Hg|\frac{1}{10}\ M\ KCl\ Hg_2Cl_2$, can be calculated as follows:[4]   The double cell,

$$\overset{\longrightarrow}{\underset{E_1 \qquad\qquad\qquad\qquad E_2}{H_2|HCl\ 0.1\ M,\ Hg_2Cl_2|Hg\ |\ Hg_2Cl_2,\ HCl\ act.\ 1|H_2,}}$$
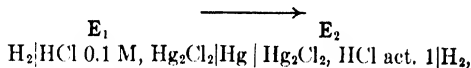
would have the electromotive force:

$$E_2 - E_1 = \frac{2\,RT}{F} \log \frac{C_2\alpha_2}{C_1\alpha_1},$$

or since $C_2\alpha_2$ is assumed $= 1$,

$$E_2 = E_1 - \frac{2\,RT}{F} \log C_1\alpha_1 = 0.3989 - 2 \times .05916 \times \log 0.0814,$$

since the square root of the product of the activities of hydrogen and chlorine ions in 0.1 molar solution is 0.814. (See Table 17.) Therefore,

$$E_2 = 0.2700\ volt\ for\ the\ e.m.f.\ of\ the\ cell,$$
$$Pt,\ H_2|H^+,\ Cl^-\ act.\ =\ 1,\ Hg_2Cl_2|Hg,$$
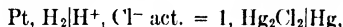
which is the potential difference of the calomel electrode in hydrochloric acid whose ions have unit activity.

[1] Lewis and Randall, *Thermodynamics*, p. 407 (1923).
[2] Abhandlungen der deutschen Bunsen Gesellschaft, No. 5 (1911); Lewis and Randall, *Thermodynamics*, p. 404 (1923).
[3] Lewis, Brighton, and Sebastian, J. Am. Soc. **39**, 2245 (1917).
[4] Lewis and Randall, *Thermodynamics*, p. 405 (1923).

Therefore the electrode $Hg|Hg_2Cl_2$, H^+, Cl^- (act. $= 1$) $= 0.2700$ volt. To find the electrode potential of the tenth-normal electrode:

$$Hg|Hg_2Cl_2, \tfrac{1}{10} \text{ M KCl},$$

imagine the cell,

$$Hg|Hg_2Cl_2, \tfrac{1}{10} \text{ M KCl}|H^+, Cl^- (\text{act.} = 1), Hg_2Cl_2|Hg,$$
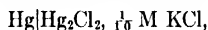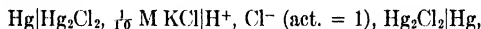
constructed with elimination of the potential at the liquid junction. Then the e.m.f. of this cell,

$$E = x - 0.2700 = RT \log \frac{1}{\text{act. } Cl^- \text{ in } \tfrac{1}{10} \text{ M KCl}}.$$

From Table 18 the activity of Cl^- in $\tfrac{1}{10}$ M KCl $= .0794$.

Therefore $x = 0.2700 - 0.05916 \log 0.0794 = 0.3351$ volt.

These and other working electrodes are given in Table 22.

TABLE 22. ELECTRODE POTENTIALS OF REFERENCE ELECTRODES REFERRED TO THE MOLAL HYDROGEN ELECTRODE AS ZERO.

Lewis and Randall, *l.c.*, p. 406.

$Hg\|Hg_2Cl_2$, n-KCl, 0.1-n-KCl[1]	$+ 0.2822$
$Hg\|Hg_2Cl_2$, 0.1-n-KCl	$+ 0.3351$
$Ag\|AgCl$, Cl^- act. $= 1$	$+ 0.2245$
$Hg\|Hg_2SO_4$, SO_4^{--} act. $= 1$	$+ 0.6213$
$Pt\|H_2,OH^-$ act. $= 1$	$- 0.8280$
$Hg\|HgO$, OH^- act. $= 1$	$+ 0.0984$

In using the hydrogen electrode in the laboratory as a working electrode it is not necessary to have the hydrogen ions with molal activity equal unity. Normal hydrochloric acid, for example, could be used and the results calculated to exactly molal activity. In using any gas electrode, the barometric pressure must be read and the vapor pressure of the solution must be taken into account in reducing the partial pressure of the gas to one atmosphere.

Determination of Single Potentials. — In using a standard electrode it is always necessary to know the direction in which the current flows through the cell, in order to find the potential difference of the other electrode. If the cell is written down and arrows drawn to show the direction of the current through it and the direction in which the standard electrode tends to send the current, it is evident at once whether the two values have to be subtracted or added to give the value of the unknown. If the sign is that of the charge on the electrode, the formula,

$$E_{cell} = E_{+pole} - E_{-pole}, \tag{46}$$

[1] Including the potential difference at the liquid junction, Lewis and Randall, J. Am. Ch. Soc. **36**, 1969 (1914).

gives the correct sign and numerical value, when any two of the three quantities are known. Of course the liquid potential differences must be allowed for if large enough to affect the result.

For example, if it is desired to find the single potential difference of copper dipping in normal copper sulfate, the cell,

$$\overline{\xrightarrow{}0.0322}$$
$$\mathrm{N.E.}\big|\,n\text{-}\mathrm{CuSO_4}\big|\mathrm{Cu}$$
$$\xleftarrow{}$$
$$.0560$$
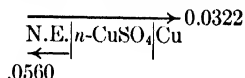
would be measured. As indicated, the cell has the electromotive force 0.0322 volt, and copper is the positive pole. Since the potential difference of the normal electrode is in the opposite direction from that of the cell, evidently the copper electrode has a potential difference 0.592 volt larger than the normal electrode and the sign is positive.

Problem 1. Find the single potential differences of the unknown electrodes in the following cells, all written with the positive pole to the right.[1]

Cell e.m.f.

Pt + H$_2$|0.02-n-HCl, 0.5-n-KCl|0.5-n-KCl, Hg$_2$Cl$_2$|Hg,   0.407.
1 atm.
$$\xrightarrow{}$$
$$0.576$$

Pt + H$_2$, 1 atm.|0.03-n-H$_2$SO$_4$|0.1-n-KCl, Hg$_2$Cl$_2$|Hg 0.434.
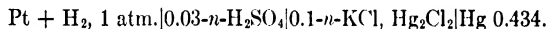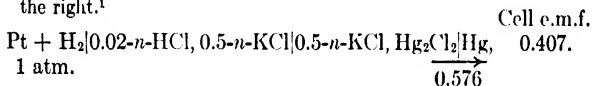
Electromotive Force and Chemical Equilibrium. — The formulas derived above make it possible to calculate the electromotive forces of voltaic cells from the equilibrium of the reaction furnishing the current, and conversely the equilibrium can be calculated from electromotive force; for if the reaction for which (31) was deduced takes place in a voltaic cell,

$$- \Delta F = \nu\mathbf{E}F = RT \log K. \tag{47}$$

Suppose the cell is considered to have the substances at equilibrium concentrations; there is then no tendency for the reaction to proceed and the electromotive force is zero. Then if $\mathbf{E}_1^\circ$ is the molal potential of the positive pole and $\mathbf{E}_2^\circ$ that of the negative pole,

$$0 = \mathbf{E}_1^\circ + \frac{RT}{\nu F} \log \frac{(E_1^{e_1})(F_1^{f_1})\, \cdots}{(A_1^{a_1})(B_2^{b_2})\, \cdots} - \left(\mathbf{E}_2^\circ + \frac{RT}{\nu F} \log \frac{(E_2^{e_2})(F_2^{f_2})\, \cdots}{(A_2^{a_2})(B_2^{b_2})\, \cdots}\right),$$

which gives,

$$\mathbf{E}_1^\circ - \mathbf{E}_2^\circ = \frac{RT}{\nu F} \log \frac{(E_2^{e_2})(F_2^{f_2})\, \cdots\, (A_1^{a_1})(B_1^{b_1})\, \cdots}{(A_2^{a_2})(B_2^{b_2})\, \cdots\, (E_1^{e_1})(F_1^{f_1})\, \cdots}. \tag{48}$$

[1] See Abhandlungen der deutschen Bunsen Gesellschaft, No. 5 (1911).

Since the term following the logarithm is the equilibrium constant of the whole reaction, (48) is the same as (47).

In substituting in (48), the reactions both at the anode and cathode are written as in (34), and the cathode reaction is subtracted from the anode reaction.

The following examples illustrate the use of these formulæ.

(1) It is desired to find the electromotive force of the cell,

$$Sn \text{ (solid)}|Sn^{++} \text{ molal sol.}|Pb^{++} \text{ molal sol.}|Pb \text{ (solid).}$$
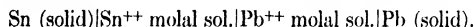
On shaking metallic lead and tin in a solution of the perchlorates of these metals it is found that,

$$\frac{Sn(ClO_4)_2}{Pb(ClO_4)_2} = 2.98 \pm 0.02,$$

and assuming the ionizations of the two salts equal,[1]

$$\frac{Sn^{++}}{Pb^{++}} = 2.98.$$

The fact that at equilibrium tin is the more concentrated ion shows tin is the negative pole of the cell. Substituting in (48),

$$\mathbf{E_{Pb}} - \mathbf{E_{Sn}} = \frac{RT}{2\,F} \log \frac{Sn^{++}}{Pb^{++}} = 0.0140 \text{ volt.}$$

Problem 2. Calculate the concentration of zinc to copper ions in a Daniell cell for which the electromotive force is zero.

$$Ans. \quad \frac{Zn^{++}}{Cu^{++}} = 10^{38}.$$

NOTE. — It is possible by adding some salt forming a complex ion with copper, to reduce the concentration of copper ions so greatly that this cell even reverses its polarity, and the question is whether such small concentrations as here calculated can really determine the potential difference. If the zinc solution is molal with respect to zinc ions, then the copper solution would be 10^{-38} molal, or one gram-mol in 10^{38} liters. Taking the Avogadro number roughly as 10^{23}, it is evident there would be only one ion to every 10^{15} liters, so that in the small quantity of solution used to determine potential differences there would be no copper ions. Ostwald attempted to overcome this difficulty by assuming that ions do not exist continuously as ions, but change back and forth from the ionized to the un-ionized state, and that these small numbers represent the fractional part of the time during which a given atom exists as an ion. Haber[2] showed, however, that this idea leads to the result that the transfer of the electric charge from ion to neutral molecule must proceed with a velocity about a million times as great as the propagation of an

[1] Noyes and Toabe, J. Am. Ch. Soc. **39**, 1537 (1917).
[2] Z. Elektroch. **10**, 433 (1904).

electric impulse, which is the same as the velocity of light, and therefore this explanation is also impossible. The calculation shows that ions in concentrations down to about 10^{-14} can actually determine electrode potentials, for at this concentration the volume too small to contain a single ion would be microscopic. Haber therefore concludes that, for example, in a silver cyanide solution a silver electrode potential corresponds to the reaction,

$$Ag + 3 CN^- + F = Ag(CN)_3^{--}$$
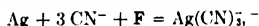
and the electromotive force is given by the equation,

$$E = E^\circ + RT \log \frac{(Ag(CN)_3^{--})}{(CN^-)^3},$$

in place of

$$Ag + F = Ag^+$$
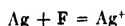
and

$$E = E^\circ + RT \log (Ag^+).$$

These small values may be considered the concentrations which would give the measured potential differences if they actually determined these values.

(2) The dissociation pressure of chlorine in lead chloride can be found by measuring the electromotive force of the cell,

$$Pb|PbCl_2, \text{ sat. sol.}|Cl_2 \text{ (1 atm.).}$$
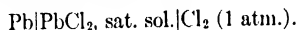
This gives the free-energy decrease of formation of one mol of lead chloride. The formation can also take place reversibly by allowing the chlorine to expand until its pressure equals that of chlorine in lead chloride ; then lead and chlorine unite without any further change in free energy. Therefore,

$$2 EF = RT \log \frac{1}{p},$$

where p is the equilibrium pressure. This can also be obtained by substituting in (31). From $E = 1.63$, $\log p = -\dfrac{1.63}{0.029} = -56$, and $p = 10^{-56}$ atm.

(3) The electromotive force of the cell,

$$H_2, \text{ 1 atm.}|H_2O|O_2, \text{ 1 atm.,}$$
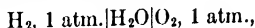
has been calculated from the dissociation of saturated water vapor at room temperature. This dissociation is calculated from measurements at higher temperatures. In this cell the reaction is,

$$2 H_2 + O_2 = 2 H_2O,$$
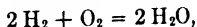
and

$$K = \frac{(H_2O)^2}{(H_2)^2(O_2)},$$

where the parentheses mean equilibrium pressures. Substituting in (32) gives,

$$E = \frac{RT}{4\,F}\left\{ \log \frac{(H_2O)^2}{(H_2)^2(O_2)^2} - \log \frac{p_{H_2O}^2}{p_{H_2}^2\,p_{O_2}} \right\}.$$

But $p_{H_2O} = (H_2O)$, and $p_{H_2} = p_{O_2} = 1$ atm.

Therefore,
$$E = \frac{RT}{4\,F}\log\frac{1}{(H_2)^2(O_2)}.$$

Substituting in $(H_2) = 3.34\ 10^{-29}$ and $(O_2) = 1.67\ 10^{-29}$ atmosphere,[1]

$$E = 0.0144 \log 5.35\ 10^{85} = 1.235 \text{ volt.}$$

Nearly the same value has been calculated for this cell by Lewis[2] and by Brönsted[3] by indirect methods. If the electromotive force of the cell is measured directly, only 1.08 to 1.15 volts are found. It is therefore evident that the true electromotive force of this cell has never been observed directly. It is probable that the oxygen electrode gives the potential of some oxide of platinum in place of that of pure oxygen.

(4) Electromotive force measurements are an important method of determining transition points. For example, $ZnSO_4.7H_2O$ has a transition point at 39°; if heated above this, the reaction,

$$ZnSO_4 \cdot 7\ H_2O \xrightleftharpoons{} ZnSO_4 \cdot 6\ H_2O + H_2O,$$
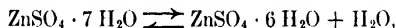
takes place from left to right. Suppose a cell is made as follows:

$$\text{Zn}\left|\begin{array}{c}ZnSO_4 \cdot 7\ H_2O\\ \text{sat. sol.} +\\ \text{crystals}\end{array}\right|\begin{array}{c}ZnSO_4 \cdot 6\ H_2O\\ \text{sat. sol.} +\\ \text{crystals}\end{array}\right|\text{Zn.}$$
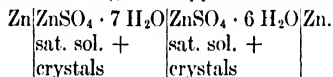
Below 39° the current in the cell must go in the direction to use up hexahydrate and form heptahydrate; that is, it must flow in the cell from left to right as it is written. Above 39°, the current is reversed. The transition point, where the two hydrates are in equilibrium, is where the current is zero.[4]

(5) Another example is the transition point from ordinary tin to gray tin. If the cell,[5]

White Tin|Sol. of Tin Salt|Gray Tin,
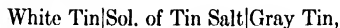
is measured below 20°, the current in the cell is from left to right;

[1] Nernst, *Theoretische Chemie*, 8–10 ed. p. 829 (1921).
[2] Z. phys. Ch. **55**, 449 (1906).
[3] Z. phys. Ch. **65**, 84 (1909).
[4] Findlay, *The Phase Rule and Its Applications*, p. 300 (1904).
[5] Cohen, Z. phys. Ch. **30**, 623 (1899).

above 20°, from right to left. This is therefore the transition point for white and gray tin.

Electrode Potentials in Fused Electrolytes. — It is found that the electromotive forces of cells of the type,

$$Ag|AgNO_3 \text{ in } NaNO_3|AgNO_3 \text{ in } NaNO_3|Ag,$$
$$C_1 \qquad\qquad C_2$$
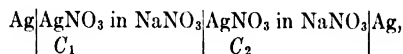
agree with the Nernst formula when the silver nitrate did not exceed a concentration of half normal.[1] In computing these cells it was assumed that the ratio of the concentrations of silver ions is the same as that of silver nitrate, from the following considerations: the mass action law for the dissociation of silver nitrate gives,

$$\frac{(Ag)(NO_3)}{(AgNO_3)} = \text{constant.}$$

In dilute solutions the NO_3 ions resulting from the dissociation of silver nitrate are negligible with respect to those from the solvent, therefore $(NO_3) = \text{constant}$, and

$$\frac{(Ag)}{(AgNO_3)} = \frac{(Ag)}{(Ag) + (AgNO_3)} = \text{constant.}$$

Since $(Ag) + (AgNO_3) = C$, the total concentration of the salt, the above assumption that

$$\frac{(Ag)_1}{(Ag)_2} = \frac{C_1}{C_2}$$

is reached. Table 23 gives some of the results.

TABLE 23. ELECTROMOTIVE FORCES OF CELLS OF THE TYPE

$$Ag|AgNO_3 \text{ IN } NaNO_3|AgNO_3 \text{ IN } NaNO_3|Ag$$
$$C_1 \qquad\qquad C_2$$
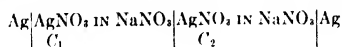
EQUIVALENT CONC. OF AgNO AT 400° C		TEMPERATURE	E OBSERVED	$E = \frac{RT}{F} \log \frac{C_1}{C_2}$	DIFFERENCE
C_1	C_2				
0.00986	0.06206	350	− 0.1014	− 0.0896	+ 0.0028
0.00986	0.1220	337	− 0.1335	− 0.1320	+ 0.0015
0.06206	0.1220	349	− 0.0370	− 0.0362	+ 0.0008
0.5565	0.00986	340	+ 0.2094	+ 0.2130	− 0.0036

[1] Goodwin and Wentworth, Physical Review, **24**, 77 (1907).

These results indicate also that the mass action law applies to the dissociation of fused salts in much higher concentrations than in aqueous solutions.[1]

Sackur also finds that the laws of dilute solutions apply to the electromotive force of concentration cells up to normal concentration with an accuracy of one percent, both for the dissociated and for the undissociated parts.[2]

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M. Le Blanc, *Lehrbuch der Elektrochemie*, 9th and 10th ed., 1922, Oscar Leiner, Leipzig.

[1] See also Lorenz, *Elektrolyse Geschmolzener Salze* (1906).
[2] Z. phys. Ch. **83**, 290 (1913).

CHAPTER VI

POLARIZATION AND ELECTROLYSIS

THE principal subject of the preceding chapter was the inherent potential differences that exist between electrode and solution when only an infinitesimal current is flowing. The present chapter will discuss the closely related subjects of potential differences at electrodes through which an appreciable current is flowing, impressed from an external source, and the products of electrolysis.

In the cyclical process used in the derivation of the Nernst equation,

$$E = \frac{RT}{\nu F} \log \frac{P}{p},$$

a current is supposed to pass across the boundary between the electrode and solution, first in one direction, and then in the other. This equation should therefore be independent of the direction in which the current flows; the only condition imposed is that the process should be reversible; that is, the current is supposed so small that no appreciable change takes place in or around the electrode. Thus the electromotive force of a Daniell cell is the same, whether a minute current is taken from it as a voltaic cell, or if such a current is sent through it in the opposite direction as an electrolytic cell.

The fact that, as was to be expected, the Nernst equation does apply to electrolytic cells for small currents was shown experimentally by Le Blanc.[1]

When, however, an appreciable current is passing across the boundary between electrode and solution, the value of the potential difference between the two is changed from its equilibrium value given by the Nernst equation. The difference between these two values is called *polarization*. Complete or partial removal of this difference is called *depolarization*, and any agent which produces depolarization is called a *depolarizer*. The verb *polarize* is used

[1] Z. phys. Ch. **8**, 299 (1891); **12**, 333 (1893).

in the sense of applying an external electromotive force to an electrode or electrolytic cell.

Concentration Polarization. — One cause of polarization that at once suggests itself is the change in concentration that takes place on electrolysis. Suppose a metal is depositing on a cathode. Since the ions are not transported as rapidly as they are removed by electrolysis, p is diminished, and the value of **E** increases. If the cathode, at which the solution becomes diluted and consequently lighter, is placed horizontally above an anode of the same metal, there will be no convection currents, and ions will be brought to the cathode only by transference and diffusion. Consequently, on applying an electromotive force, the current must fall to such a value that the number of ions it removes are replaced by transference and diffusion. This is called a *residual current*. There is a gradual change in the concentration of the solution from the electrode to the original concentration which still exists at a distance from the electrode determined by the conditions of the electrolysis, such as temperature, diffusion constant of the salt, and current. This layer of variable concentration is called a *diffusion layer*. There is always such a layer, no matter how thoroughly the solution may be stirred.

The same relations hold for stirred solutions and vertical electrodes, but in this case much larger currents are possible. These larger currents are not called residual currents, though in aqueous solution all currents which do not decompose water belong to the same class and differ only in degree.

If the current is so large that the concentration of metal ions on the cathode surface is reduced practically to zero, no larger current can pass however the potential difference may be increased, unless some other ion begins to deposit. This current is called the *limiting* or *maximum current*. It evidently depends on the concentration, temperature, and rate of stirring of the solution.

Similar considerations apply to the anode. Here also there is a limit to the current under given conditions. If the current is so large that the solution becomes saturated, salt crystallizes on the anode and either stops the current or causes the potential difference to rise to the point where other ions are discharged.

The rate of change of concentration clearly depends on the area of the surface on which the current acts. Therefore, to make results comparable, the current is given as the number of amperes per unit surface or as the current density.

Since the potential difference between electrode and solution

is changed by the passage of a current, and by different amounts depending on the value of the current, *equilibrium* potentials give no information as to what takes place at the electrode in electrolysis.   In case there were no polarization, they would do so, for that ion is deposited first which is the most easily deposited. It is therefore necessary to know the potential difference for each current density for the electrode and ion in question.   This relation is conveniently represented by current-density-potential graphs, in which current density is usually plotted as ordinates, potential difference as abscissæ.

In order to measure the potential difference between electrode and solution when a current is flowing, the tube leading to the
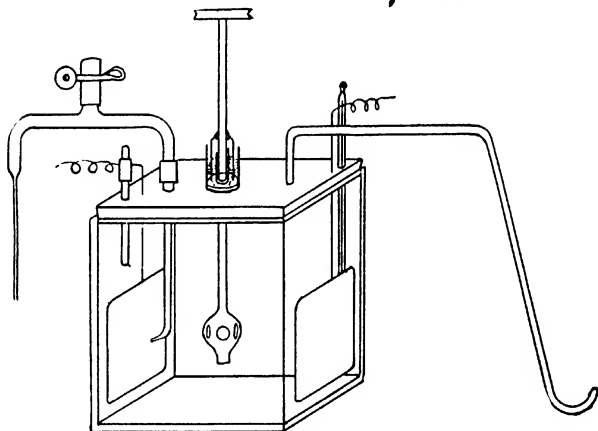
FIG. 29

normal electrode is pressed against the side of the electrode to be measured which faces the other electrode of the electrolytic cell, as shown in Figure 29.   The current density should be as uniform as possible, to secure which no current should reach the reverse side of the electrode measured.   This can be accomplished by pressing the electrode against the cell wall or by insulating with paraffine.

CHEMICAL POLARIZATION

Chemical Polarization. — It was formerly supposed that concentration polarization, described above, is the only polarization

at reversible electrodes. It has since been found, however, that *nearly all substances have greater polarization than can be accounted for by concentration changes alone.* This was shown conclusively by Le Blanc by oscillograph experiments.[1]

The movable coil of an oscillograph was connected in parallel with the experimental cell and a commutated direct current passed through the cell. This current passed in one direction for 0.018 second, was broken for the same period, and was then reversed for the same period. When the curcuit is closed, the deflection of the spot of light reflected from the mirror attached to the movable coil is a measure of the potential difference between the electrodes of the experimental cell. According to the direction of the current, this will be above or below the axis, or line traced on the photographic paper when there is no deflection. The distance from the zero axis will be proportional to the sum of the polarization and the IR drop in the cell. When the circuit is broken, the cell discharges through the movable coil and this deflection is a measure of the polarization of the cell.

If there is no polarization, as in the case of iodide-iodine solutions, the deflection is a straight line parallel to the axis and

$$Cu \mid n\text{-}Cu\,SO_4 \cdot n\text{-}H_2SO_4 \mid Cu$$
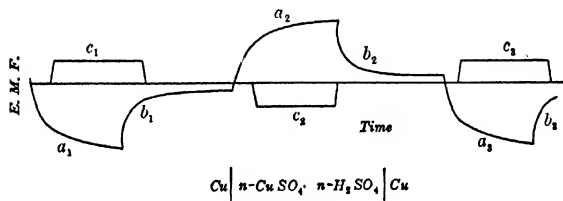
FIG. 30

its distance from the axis is a measure of only the IR drop through the cell, and when the circuit is broken there is no deflection. Figure 30 shows the results with acid copper sulfate solution where there is polarization. The curves a_1, a_2, etc., represent the polarization of the cell when a constant current is applied, while b_1, b_2, etc., show the polarization when the current is broken. For calibration, the lines c_1, c_2, etc., are taken when the cell is replaced by a wire of the same resistance as the cell, and with the same current. The maximum value of the polarization is found from this. Thus if 1 mm. distance from the axis = 0.00030 amp.

[1] Abhandlungen der deutschen Bunsen Gesellschaft, No. 3 (1910).

and if the maximum distance is 10 mm., the current is 0.0030 amp. This multiplied by the sum of the resistances of the movable coil and the adjustable resistance in series with it gives the potential difference at the electrodes. If this resistance is 203 ohms, the polarization is 0.609 volt. The results showed great variation in the polarization, while if the polarization had been due only to concentration polarization all the values would have been small and about equal. The results show, therefore, that the reactions in general do not go with unlimited velocity. This is called *chemical polarization.*

Since electrochemical processes consist of more than one step, the attempt has been made to find to which of these this polarization is due. The following are some of ·the theories proposed: (1) The ionization of the salt may not take place with unlimited velocity. In this case ions would not be furnished by the undissociated salt as rapidly as they are removed by electrolysis, and their concentration would fall below equilibrium concentration.

(2) There may be a resistance to the transfer of the electric charge, corresponding to the step,

$$M + \nu F = M^{\nu+}.$$
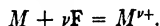
This would require energy in the form of excess potential difference.

(3) The value of the electrolytic solution pressure P in the Nernst equation may be increased in some way above the equilibrium value. This applies especially to gases.

Cathodic Processes

Hydrogen Evolution. — The deposition of hydrogen is the most important of all cathode reactions from a theoretical point of view, since this ion exists in all aqueous solutions.

If a platinized platinum electrode is polarized only a minute amount in excess of the potential difference that exists between platinized platinum in contact with gaseous hydrogen, hydrogen bubbles appear. If the current density is increased, a small polarization occurs, due entirely to concentration change. Hydrogen therefore forms a reversible electrode in contact with platinized platinum.

It is found that an excess voltage is required to liberate hydrogen on all other metals than platinum except palladium. The difference between this voltage and the reversible electromotive force of hydrogen is called *overvoltage.* This quantity has been determined in two ways: (1) as the potential difference at which the

first bubble appears, and (2) by the kink in the current-density-potential curve. The former gives higher values, as shown in Table 24.

TABLE 24. OVERVOLTAGES FOR HYDROGEN [1]

METAL	CASPARI	COEHN AND DANNENBERG	THIEL AND BREUNING ROUGH SURFACES
Platinum, platinized . . .	0.005	0.0	0.0
Platinum, smooth	0.09	——	——
Palladium	0.46	− 0.26	0.0
Gold	0.02	0.05	0.165
Silver	0.15	0.07	0.097
Nickel	0.21	0.14	0.1376
Copper	0.23	0.19	0.135
Iron in NaOH	0.08	0.03	0.087
Retort carbon	- ——	——	0.1428
Graphite	——	——	0.336
Aluminum	——	0.27	- ·--
Cadmium	0.48	——	——
Tin	0.53	——	——
Indium	——	- · · ·	0.533
Lead	0.64	0.36	——
Zinc	0.70	—— ——	——
Mercury	0.78	0.11	–

The potential difference for an electrode on which hydrogen is being liberated must therefore be expressed by the equation,

$$E = \frac{RT}{F} \log \frac{P}{p} + \eta_H, \qquad (1)$$

where η_H represents the overvoltage. This depends not only on the kind of metal, but also on the physical state of the surface, the temperature, and the pressure. An increase in temperature reduces overvoltage.[2] The kink point is independent of pressure;[3] the bubble point is not affected much between pressures of 40 and 100 centimeters of mercury; below this the overvoltage increases rapidly.[4]

[1] Caspari, Z. phys. Ch. 30, 89 (1899). First appearance of bubbles. Coehn and Dannenberg, Z. phys. Ch. 38, 609 (1901). Kink point in voltage current curve. Thiel and Breuning, Z. anorg. Ch. 83, 329 (1913). First appearance of bubbles.

[2] Knobel and Joy, Tr. Am. Electroch. Soc. 44, 443 (1923).

[3] Wulf, Z. phys. Ch. 48, 87 (1909).

[4] Goodwin and Wilson, Tr. Am. Electroch. Soc. 40, 173 (1921).
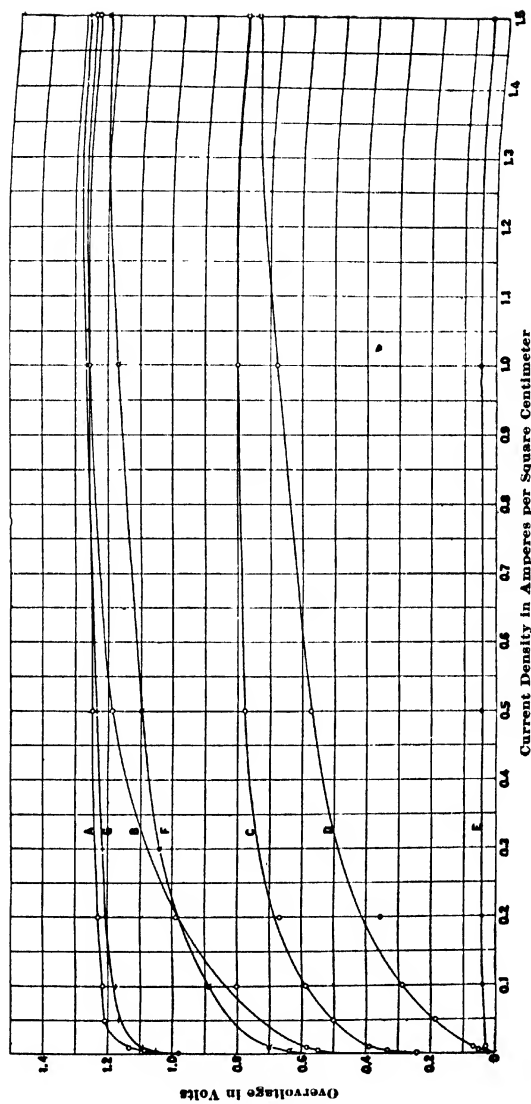
FIG. 31. — HYDROGEN OVERVOLTAGES DETERMINED IN 2-n-H$_2$SO$_4$: A, CADMIUM; B, COPPER; C, GOLD; D, SMOOTH PLATINUM; E, PLATINIZED PLATINUM; F, CARBON; G, LEAD

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Current Density in Amperes per Square Centimeter
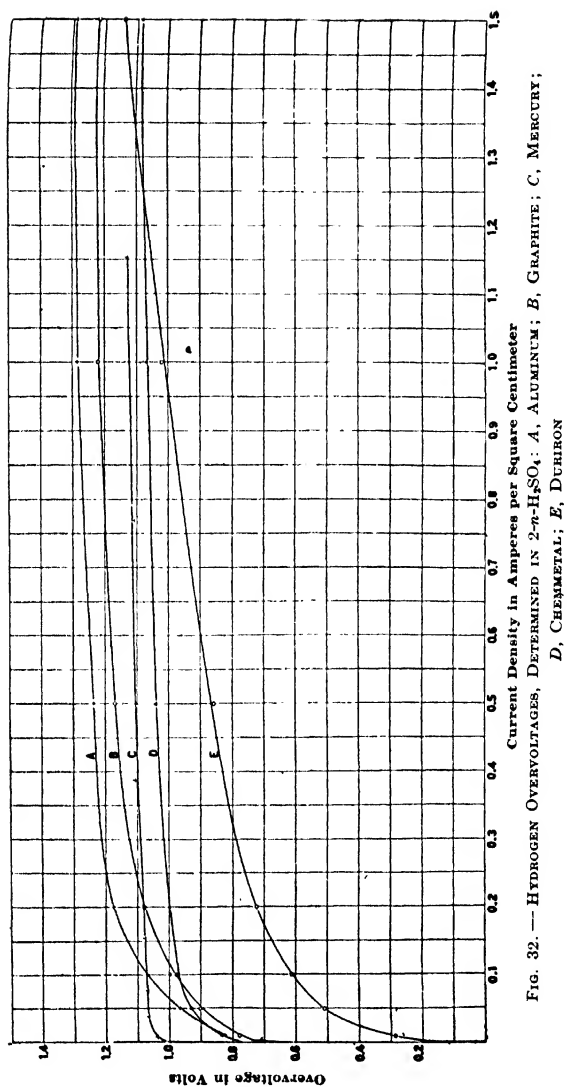
Fig. 32. — Hydrogen Overvoltages, Determined in 2-*n*-H₂SO₄: *A*, Aluminum; *B*, Graphite; *C*, Mercury; *D*, Chemmetal; *E*, Duriron

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Hydrogen overvoltage is reduced by superimposing an alternating current on the direct current.[1]

For electrolyses it is important to know the overvoltages at higher current densities. These are shown in Figures 31 and 32 for a number of metals.[2] The metals were of high purity, but the surfaces were not polished.

Since the deposition of hydrogen on metals causes roughening of the surfaces, the position of current-density-voltage curves changes with time, and also depends on the previous history of the electrode; that is, the current density with which it has been previously polarized.

The extra energy required to deposit hydrogen on an electrode having overvoltage appears as heat. This would be expected, and it has been confirmed by experiment. A current was sent through two cells identical in all respects except that the cathode in one was lead and platinized platinum in the other. The anodes were platinum, the electrolyte sulfuric acid of 1.2 specific gravity, and the water equivalents of the two cells were made equal. The cathode potentials were measured against tenth-normal electrodes, and the temperature rises in the cells were determined. The difference in the rises in temperature in the two cells is then due only to the difference in the quantities of heat produced at the two cathodes. The following results were obtained:[3]

EXPERIMENT NUMBER	DIFFERENCE IN VOLTAGE CALC FROM DIFFERENCE IN HEAT DEVELOPED	DIFFERENCE IN VOLTAGE MEASURED vs. 0.1-n-KCl ELECTRODE
1.	0.913	0.950
2.	0.600	0.597

Overvoltage is supposed to be due to an increase in the electrolytic solution pressure P in the Nernst equation, by the formation of a hydride with the metal of the electrode of greater free-energy content than gaseous hydrogen. This is case (3) above. It cannot be due to different catalytic effects of the cathode material on the ionization of hydrogen, because many other facts indicate that this is nearly instantaneous. It is also improbable that the

[1] Goodwin and Knobel, Tr. Am. Electroch. Soc. **37**, 617 (1920).

[2] Knobel, Caplan, and Eiseman, Tr. Am. Electroch. Soc. **43**, 55 (1923). See also Tafel, Z. phys. Ch. **50**, 641 (1904).

[3] Kaufler, Z. Elektroch. **13**, 633 (1907). See also J. W. Richards, Tr. Faraday Soc. **9**, 140 (1913).

higher pressure existing in the small bubbles when first formed on the cathode can account for more than a small amount of over-voltage, for if the pressure were high enough to account for the overvoltage of mercury, according to equation (37), Chapter V, the gas would have to be under a pressure of 10^{33} atmospheres, which is absurd. The hydride theory therefore seems
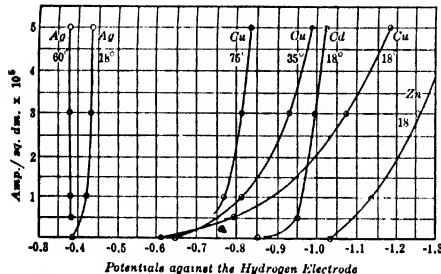
FIG. 33. — METAL OVERVOLTAGES. SOLUTIONS $\frac{1}{10}$ MOL AgNO$_3$, $\frac{1}{10}$ MOL KCN PER LITER; $\frac{1}{10}$ MOL CD(CN)$_2$, $\frac{1}{10}$ MOL KCN PER LITER; $\frac{1}{10}$ MOL CuCN, $\frac{2}{10}$ MOL KCN PER LITER

to offer the most satisfactory explanation at the present time.[1]

The effect of colloids on overvoltage is very slight. The addition of 0.1 percent of gelatin increases the overvoltage on lead by
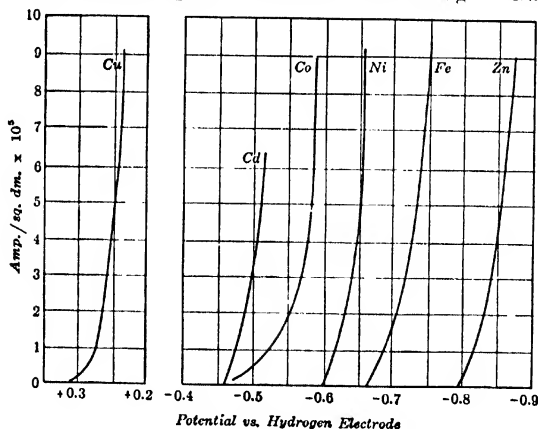
FIG. 34. — METAL OVERVOLTAGES. NORMAL SULFATE SOLUTIONS. CD SOLUTION HAS ALSO 10 PERCENT H$_2$SiF$_6$

[1] For an extensive discussion of this subject see Foerster, *Elektrochemie wässeriger Lösungen* (1922). Also Newbury, J. Ch. Soc. **109**, 1359 (1916).

0.05-volt.[1] According to other experiments[2] a maximum hydrogen overvoltage occurs as the concentration of the colloid consisting of gelatin or gum arabic is increased. This maximum is independent of the nature of the electrode. This is explained as due to the change in the concentration of the hydrogen ions by the colloid, by the formation of adsorption compounds.

The Deposition of Metals. — Current-density-voltage curves for a number of metals are given in Figures 33, 34, and 35.[3] These were all obtained in well-stirred solutions.

It is clear that in most cases there is considerable chemical polarization, otherwise the curves would all be as close to the vertical as those of mercury and lead. Stirring tends to eliminate concentration polarization, so that departure from the vertical is principally due to chemical polarization.

Fig. 35 — Metal Overvoltages

It is therefore clear that the electrode potential of cathodes must be represented by the equation,

$$E = \frac{RT}{F} \log \frac{P}{p} + \eta_M, \qquad (2)$$

where η_M is the overvoltage for the metal deposition.

[1] Marie, C. R. **147**, 1400 (1909).

[2] Isgarischew and Berkmann, Z. Elektroch. **28**, 47 (1922).

[3] Foerster and Cofetti, B. B. **38**, 2934 (1905); Foerster, Z. Elektroch. **13**, 561 (1907); Schildbach, Z. Elektroch. **16**, 967 (1910); Schweitzer, Z. Elektroch. **15**, 602 (1905); Foerster's *Elektrochemie wässeriger Losungen*, for results of unpublished work; Foerster, Abhandlungen der deutschen Bunsen Gesellschaft, No. 2 (1909),

It is an interesting point that large values of η_H are associated with small values of η_M in the same metal, as for example in lead and mercury, while small values of η_H are associated with large values of η_M, as with the iron group. [1]

Complex salts generally show greater chemical polarization than simple salts of the same metal. An example of this is shown by the curves for copper sulfate and for potassium cuprous cyanide. In the case of the copper cyanide complex, more time is required for ionization, and the polarization due to this cause is added to that due to the transfer of the electric charge. Independent evidence that time is required for the cuprous ion to enter the potassium copper cyanide complex, and presumably also to ionize from it, is furnished by the experiments of Le Blanc and Schick, as follows.[2] With a sufficient excess of potassium cyanide, a direct current deposits only hydrogen at the cathode because of the small number of copper ions. At the anode, however, copper goes into solution quantitatively. Therefore, on electrolyzing with an alternating current, any copper dissolved anodically will not be electrolyzed out when the current is reversed if it has had time to enter the complex. If, however, the current is reversed before the ion has had time to enter the complex, it will be deposited at the next reversal of the current, and the current efficiency of dissolving copper will decrease. Experiments showed that with less than 1000 alternations per minute copper dissolved with 100 percent efficiency, but fell to less than 40 percent for 30,000 alternations. Le Blanc estimates that if 0.1 normal copper ions are brought in contact with between 1 and 4 normal potassium cyanide, all copper is combined with cyanide in 0.06 second, while if the concentration of copper ions is $\frac{1}{800}$ normal after 0.008 second the reaction has hardly begun. The relation between these velocities and polarization has not, however, been worked out quantitatively to see whether reaction velocities of this order of magnitude would account for appreciable polarization.

The iron group of metals are examples where there is considerable polarization even when deposited from simple salts. This may be partly due to the retardation of the splitting up of hydrated ions according to a reaction such as the following:

$$Ni(H_2O)_n^{++} = Ni^{++} + nH_2O,$$
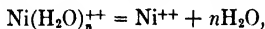
or the dehydration may take place after the hydrated ion has been

[1] Foerster, *Elektrochemie wässeriger Lösungen*, p. 456 (1922).

[2] Z. Elektroch. **9**, 636 (1903).

deposited.[1]   But this is not the only cause of polarization in these cases, since it is found that foreign substances in the electrode, such as hydrogen and zinc, increase the polarization considerably, showing that the electrode is partly responsible.[2]

The polarization of copper deposition from copper sulfate is very much increased by the presence of sulfuric acid or of neutral salts.[3]

Whether a metal will be deposited from aqueous solutions depends on the relative values of the potentials,

$$\mathbf{E}_M = \frac{RT}{\nu \mathbf{F}} \log \frac{P_M}{p_M} + \eta_M \text{ and } \mathbf{E}_H = \frac{RT}{\mathbf{F}} \log \frac{P_{H_2}}{p_{H^+}} + \eta_H,$$

for the solution and current density in question. If (1) for all current densities $\mathbf{E}_H$ is more negative than $\mathbf{E}_M$, only metal will deposit. The current-density-voltage curves would then be related as shown in Fig-ure 36. This applies to metals that are more no-ble than hydrogen in strong acid solutions, as long as the limiting cur-rent density for the metal is not exceeded. If it is exceeded, of course hydro-gen must deposit and the potential of the electrode jumps over to the hydro-gen curve. If (2) $\mathbf{E}_H$ is less negative than $\mathbf{E}_M$, for all current densities, hy-drogen only is deposited.

FIG. 36. — OVERVOLTAGES OF HYDROGEN AND OF METAL, SHOWING CONDITIONS FOR DEP-OSITION OF METAL ALONE

The curves in Figure 36 would then be interchanged. This ap-plies to those metals that decompose water, such as the alkali metals.

It is an interesting, though not important, question whether sodium is deposited and then reacts with water, or whether hydrogen is deposited primarily. This depends on whether hydrogen or sodium has the more negative electrode potential. According to formula (37), Chapter V, or Table 20 the electrode potential of hydrogen in normal hydroxyl ions is $\mathbf{E} = 0 + 0.059$

[1] Foerster, Z. Elektroch. **22**, 99 (1916).
[2] Freundlich and Fischer, Z. Elektroch. **18**, 886 (1912).
[3] Reichenstein and Zieren, Z. Elektroch. **19**, 531 (1913).

$\log 10^{-14} = -0.83$ volt, and in fact hydrogen can be liberated at about this potential difference on platinized platinum, showing the ionization takes place with great rapidity.

The electrode potential of sodium is -2.7 volts, and in order that sodium should be deposited it is necessary either that the electrode potential of hydrogen be increased to -2.7 volts, or that the electrode potential of sodium be reduced to -0.83, or that both be changed until they equal each other. The overvoltage of hydrogen at 10 amp./sq. dm. does not exceed 1.3 volts in acid solution, as shown by Figures 31 and 32, and if the same values are assumed for alkaline solutions, there results a possible hydrogen electrode potential of $-0.83 - 1.3 = -2.1$ volts. In order to have the deposition of sodium it would therefore be necessary to have a reduction of the sodium potential by depolarization. This happens in case sodium can alloy with the cathode, as with mercury, but otherwise the deposition of sodium probably does not take place.　•

Ordinarily it does not help to reduce the hydrogen-ion concentration by using neutral solutions for the purpose of depositing such metals as aluminum and magnesium, for if only a small amount of hydrogen is liberated, the solution becomes alkaline and the hydroxides are precipitated, but on a cathode rotating at 15,000 revolutions a minute and a high current density small amounts of aluminum can be deposited from a saturated aluminum chloride solution.[1]

If (3) $E_H = E_M$, metal and hydrogen deposit together. In this case the current-density-voltage curves would be related as shown in Figure 37, where the relative positions of hydrogen and the metal are such that the same vertical line cuts both curves. The amounts deposited at a given electrode potential will be proportional to the current densities corresponding to the intersections of the vertical and the curves M and H and the efficiency of metal deposition is $AC/AC + AB$. Nickel, zinc, and cadmium belong to this case. It is to be noted that in the case of metals that tend to dissolve in acid, the current cannot go in the direction from solution to cathode and consequently hydrogen cannot be deposited until the impressed voltage is at least equal to that with which the metal tries to dissolve.

Formation of Alloys. — Alloys are formed either when the deposited metal alloys with the cathode, as in the case of the technically important sodium amalgam, or by the simultaneous deposition of more than one metal. Mercury has a depolarizing action on sodium, as shown by the value of the potential difference between sodium amalgam containing a few tenths of a percent of sodium and a sodium hydrate solution. Referred to

[1] Tucker and Thomssen, Tr. Am. Electroch. Soc. **15**, 497 (1909).

a molal hydrogen electrode this is − 1.72 volts, one volt less than the molal potential of sodium.[1] This, with the overvoltage of hydrogen on mercury, makes the formation of this amalgam possible.

The more general way of forming alloys is to deposit two metals simultaneously. Whether the two metals deposit simultaneously depends on the relative values of their electrode potentials for the solution and current density under consideration:

$$\mathbf{E}_1 = \frac{RT}{\nu_1 \mathbf{F}} \log \frac{P_1}{p_1} + \eta_{M_1} \text{ and } \mathbf{E}_2 = \frac{RT}{\nu_2 \mathbf{F}} \log \frac{P_2}{p_2} + \eta_{M_1}.$$

If they deposit together, of course $\mathbf{E}_1 = \mathbf{E}_2$, but the current densities corresponding to these values are usually not equal. The current-density-voltage curves would be placed in the same relative positions as the hydrogen and metal curves in Figure 37.

The most important technical electrolytic alloy is probably brass. Though copper and zinc can be deposited together from sulfate solution,[2] the current density has to be above the limiting value for copper and the deposit is consequently spongy. In order to get a smooth deposit, cyanide solutions are necessary, in which the electrode potential of zinc and copper become equal. These potentials are made equal by three different causes: (1) in cyanide solutions the copper-ion concentration is reduced more than the zinc, so that the more cyanide is present, the nearer the electrode potentials approach each other. This is shown in Table 25.[3] (2) The copper current-density-voltage curve departs more from the vertical than the zinc in cyanide solution as shown in Figure 33,

FIG. 37. — OVERVOLTAGES OF HYDROGEN AND OF METAL, SHOWING CONDITION FOR SIMULTANEOUS DEPOSITION OF METAL AND HYDROGEN

[1] Haber and Sack, Z. Elektroch. **8**, 251 (1902).
[2] Sauerwald, Z. anorg. Ch. **111**, 263 (1920).
[3] Summarized in Foerster's *Elektrochemie wässeriger Lösungen*, p. 182 (1922), from work by Spitzer, Z. Elektroch. **11**, 345 (1905), and by Diethelm.

TABLE 25. EQUILIBRIUM ELECTRODE POTENTIALS OF
COPPER AND ZINC IN CYANIDE SOLUTIONS

	ELECTROLOYTE CONTAINS PER LITER			
	1 Equivalent MSO₄	$\frac{1}{10}$ Mol MCy + $\frac{1}{10}$ Mol KCy	$\frac{1}{10}$ Mol MCy + $\frac{1}{10}$ Mol KCy	$\frac{1}{10}$ Mol MCy + 1 Mol KCy
Zinc . . .	− 0.801	− 1.033	− 1.182	− 1.231
Copper . . .	+ 0.308	− 0.610	− 0.964	− 1.169

and this at higher current densities brings the electrode potential
for copper deposition still nearer that of zinc. (3) Copper has a
depolarizing effect off the deposition of zinc as shown by the fact
that brass is obtained at electrode potentials lower than the
equilibrium potential of zinc in this solution. Table 26 shows
how the current density and relative concentration of copper and
zinc affect the composition of the alloy deposited.[1]

TABLE 26. DEPOSITION OF BRASS FROM SOLUTIONS CONTAINING
$\frac{1}{10}$ MOL (ZnCy₂ + CuCy) + $\frac{1}{10}$ MOL KCy PER LITER

ZN : CU IN ELECTROLYTE	AMP /SQ DM.	PERCENT COPPER IN ALLOY, AVERAGE VALUES
1 : 1	0.27	84.1
1 : 4	12	83
1 : 1	12	63
7 : 1	5	81
7 : 1	12	46.3
12 : 1	12	21.3
31 : 1	12	10.4

The quantity of potassium cyanide also has a marked effect
on the electrolysis. If there is just enough potassium cyanide
to bring the solution to $\frac{1}{10}$ molal K_3CuCy_4 and $\frac{1}{10}$ molal
K_2ZnCy_4, the current efficiency at the cathode is only 20 percent,
and falls to zero rapidly with the addition of more potassium
cyanide. If there is only enough potassium cyanide to make the
solution $\frac{1}{10}$ molal in the simpler salt $KCuCy_2$, chemical polariza-
tion is small and the electrolytic deposition is nearly reversible
up to a current density of 0.3 amp./sq. dm.[2]

[1] Sauerwald, Z. anorg. Ch. **111**, 270 (1920).
[2] Höing, Z. Elektroch. **22**, 286 (1916), and Foerster's summary, *Elektrochemie wässeriger Losungen*, p. 496 (1922).

Though the electrode potential of zinc is more negative than copper in this solution, when the two are present together zinc in some way *polarizes* copper making its deposition more difficult so that brass is still deposited.

An increase in temperature much above 20° C. reduces chemical polarization for the metal deposition and therefore alters the relative values at which copper and zinc deposit so that copper and not brass is deposited.[1]

On account of the large value for η_M for the iron group, alloys of these metals with much less noble metals such as zinc and magnesium, are deposited from simple salts. If iron or nickel sulfate containing zinc sulfate is electrolyzed at ordinary temperatures, the deposit contains more zinc than nickel.[2] The action is rather peculiar in that first the iron metals depolarize zinc, which when in the electrode polarizes the iron metals and renders their further deposition more difficult. The proportion of zinc depositing then increases. Hydrogen also helps the polarizing effect of zinc sulfate.[3]

A solution 4-normal in magnesium and 0.5-normal in nickel sulfate gives a deposit containing about 2 percent magnesium. The deposition of magnesium is made possible by the formation of an alloy or solution of magnesium in nickel, since magnesium cannot be deposited in the pure state.[4]

Form of Metal Deposits. — The physical character of metal deposits is of great practical importance. Some of the principal forms of metal deposits are (1) isolated crystals, as silver deposited from silver nitrate ; (2) a distinctly crystalline, continuous surface, like copper from copper sulfate ; (3) a smooth surface without recognizable structure, such as copper from cyanide baths ;[5] (4) surfaces so smooth as to appear polished, as silver from cyanide baths with certain other additions ; (5) a spongy amorphous form, such as copper deposited from dilute sulfate baths at high current density ; (6) long needles or aigrettes, as lead from dilute nitrate, and tin from tin chloride, and finally (7) in a black form, the most familiar example of which is platinum from platinic chloride solution.

[1] Brunner, Dissertation, Zürich (1907); Foerster, *Elektrochemie wässeriger Lösungen*, p. 496 (1922).

[2] Toepffer, Z. Elektroch. **6**, 342 (1899).

[3] Foerster, Z. Elektroch. **22**, 93 (1916).

[4] Coehn and Siemens, Z. Elektroch. **8**, 591 (1902); Siemens, Z. anorg. Ch. **41**, 249 (1904).

[5] Sieverts and Wippelmann, Z. anorg. Ch. **91**, 1 (1916).

The conditions that determine the kind of deposit must be briefly explained.

Smee [1] pointed out that the deposition of metals is a crystallization process,[2] and crystallization consists in two steps: (1) the formation of crystal germs or nuclei, and (2) the further growth of these nuclei to form larger crystals. Each of these steps has its own velocity, and the relation between these velocities determines the character of the deposit. If nucleus formation is more rapid than crystal growth, the deposit is fine grained; if crystal growth is more rapid than nucleus formation, coarse crystals are formed. The factors that determine the values of these velocities are: (1) *the nature of the salt from which the metal is deposited.* This is shown by the fact that the same metal is deposited in entirely different forms from different salts. Silver, for example, is deposited in a smooth layer from cyanide baths, and as loose crystals from silver nitrate. The cause for the smoothness of deposits universally obtained from complex salts is that some of the complex salt deposits with the metal and prevents crystal growth in the same way that this is prevented by colloids as explained below.[3] There is also some specific influence of the anion which is not yet understood, for this explanation does not apply to the difference in the deposits of lead from lead nitrate and from lead chlorate, and to other similar cases.

(2) *The ratio of current density to concentration of metal ions at the cathode surface.* This ion concentration is not that in the body of the solution but is always less and is determined by the concentration of the body of the solution, the rate of stirring, and temperature in its effect on diffusion. Very low current density and a stationary electrolyte favor the growth of crystals rather than the formation of new crystal nuclei. A higher current density makes the formation of new nuclei necessary, because the velocity of crystal growth is not great enough to take care of all the metal deposited, and the deposit becomes finer grained. A still further increase in current density makes the nucleus formation so outweigh crystal growth that the deposit becomes loose and spongy. Thus a high value of the ratio of current density to concentration

[1] 2d ed. of Elements of Electrometallurgy, 1842, quoted by Bancroft, Tr. Am. Electroch. Soc. **21**, 239 (1912). See also Hughes, Bull. 6, Dep. of Sci. and Ind. Res. London (1922), and J. Phys. Ch. **25**, 495 (1921).

[2] The mechanism of metal deposition may consist in electrons going into the solution and discharging ions, which then crystallize like any other substance.

[3] Kohlschütter, Z. Elektroch. **19**, 181 (1913).

is analogous to sudden chilling in ordinary crystallization, and a low value of this ratio to slow cooling, for sudden cooling produces many small crystals, slow cooling, large crystals. Thorough stirring counteracts the effect of high current density in producing spongy deposits. This is shown by the fact that good deposits can be obtained in copper sulfate solutions with current densities up to 260 amp./sq. dm. on a cathode rotating at 5500 revolutions a minute,[1] while 65 amp./sq. dm. would give a loose deposit with a stationary electrolyte. In copper refining about 2.2 amp./sq. dm. is used with a slowly circulating electrolyte.

(3) *An increase in temperature* is sometimes sufficient to change a loose deposit into a dense. This may be due to a higher rate of diffusion, or an increase in the ionization velocity, or to a greater increase in the rate of crystal growth than in the rate of nucleus formation. Copper tends to form larger crystals the higher the temperature, which would indicate a greater increase in the velocity of crystal growth than of nucleus formation. The reverse is true of alkaline stannate solution: at 18° and small current density tin deposits in the form of needles, while at 90° the deposit becomes dense. This would show in this case a greater increase in the velocity of nucleus formation with the temperature than of crystal formation.[2]

(4) *The presence in solution of so-called " addition agents,"* substances which have been found to improve deposits. These are usually organic substances, and often colloids. Glue is the most commonly used for this purpose. It is used both in copper and in lead refining; one part in 4 to 8 million of solution suffices to improve the deposit. Their action probably consists in reducing the rate of crystal growth by adsorption on the surfaces of crystals, forming a thin layer which increases the resistance and causes the formation of new nuclei rather than a continued crystal growth. These additions are included in the deposit and therefore have to be replaced continuously. In the case of copper the deposit has been shown to consist of very thin alternate layers of gelatin and metal, in which crystalline structure can be detected by X-ray analysis, but not by the microscope.[3]

(5) *The valence of the metal has an effect on the form of the deposit in cases where two valences are possible.* Thus lead is

[1] Bennett, Tr. Am. Electroch. Soc. **21**, 253 (1912); also Zimmerman, *ibid.* **3**, 245 (1903).

[2] Foerster, *Elektrochemie wässeriger Lösungen*, p. 389 (1922).

[3] Grube and Reuss, Z. Elektroch. **27**, 45 (1921).

deposited from solutions containing lead only in the bivalent state in large single crystals, while the presence of quadrivalent lead causes the deposit to be spongy,[1] and tin deposited from an alkaline solution containing even a little bivalent tin is in the form of large leaves and needles, while if the deposit contains only quadrivalent tin the deposit is dense.[2]

(6) Finally *the nature of the metal itself has its effect in determining the nature of the deposit,* for the relation between the velocities of nucleus formation and of crystal growth must be different for different metals. The current-density-voltage curve is another important property in this regard. The less polarizable the metal, the greater the tendency to form single crystals, as lead and silver tend to do from nitrate solutions, for there is nothing to stop the rapid growth of crystals if their natural rate of growth is high, since the current naturally concentrates on points extending above the surface of the cathode. But if polarization increases with current density, the tendency to deposit on projecting points becomes less, more metal deposits in the spaces between crystals where the current density is lower, and the surface is smoother.[3] The reason copper deposits more evenly from acid sulfate baths than from neutral is that the polarization in acid baths is greater. (See page 119.) Since increased temperature reduces polarization, in this respect it tends to make larger crystals. Temperature therefore affects the character of the deposit by its effect on diffusion, on reaction velocity, on the relative rates of nucleus formation and crystal growth, and on polarization.

An important point with respect to electrolytic metal deposits is that the metal frequently tends to contract right after deposition. If the surface on which the metal is deposited is too rigid to allow contraction, strains are produced and the metal may crack.[4] This effect is especially noticeable in the iron group. The explanation is that the metal is deposited simultaneously with hydrogen in a dispersed state, and that the metal immediately begins to recrystallize or sinter to a more dense state. This contraction increases with current density and decreasing concentration of nickel, is small in neutral solution, but greatest at low acid con-

[1] Elbs and Rixon, Z. Elektroch. **9**, 267 (1903).

[2] Naef, Dissertation, quoted by Foerster, *Elektrochemie wässeriger Lösungen*, p. 392 (1922).

[3] Aten and Boulage, Rec. des Trav. Chim. des Payes-Bas, **39**, 720 (1920).

[4] Kohlschutter and Vuilleumier, Z. Elektroch. **24**, 300 (1918); Staeger, Helvetica Chemica Acta, **3**, 584 (1920).

centration and decreases with increasing acidity while the current yield also decreases.   Increase in temperature reduces this contraction.   If the deposit becomes crystalline, the contraction decreases.

This subject is of considerable technical importance; for example, in copper refining the starting sheets become deformed before they have become thick enough to resist the unequal strains on the opposite sides and have to be removed and straightened with wooden beaters to prevent short-circuits.

Anodic Processes

Oxygen Evolution. — If the oxygen electrode were reversible, on polarizing an anode with a gradually increasing potential difference, oxygen evolution would begin at 1.23 volts measured against a hydrogen electrode in the same solution.   If the activity of hydrogen ions in the solution is molal, this would correspond to + 1.23 volts for oxygen, but in a solution molal with respect to hydroxyl ions, a hydrogen electrode would have the potential difference

$$E = 0 + 0.059 \log 10^{-14} = - 0.83 \text{ volt,}$$

by formula (37) Chapter V.   This corresponds to a potential difference of + 0.40 volt for the oxygen electrode in molal hydroxyl ions referred to the molal hydrogen electrode as zero.   But the oxygen electrode is not reversible; like hydrogen it has overvoltages depending on the metal constituting the electrode.   On platinized platinum in 2-normal sulfuric acid a slight increase in current is found at 1.08 volts, the significance of which is not understood, but no oxygen is evolved until a potential difference of 1.50 to 1.63 volts, depending on the electrode, is reached.[1]

Table 27 contains the potentials at which oxygen begins to evolve in normal potassium hydrate on different metals, measured against a hydrogen electrode in the same solution, and the differences between these values and 1.23, which are the overvoltages.[2]

For the same metal, these values are close to those measured in acid, which indicates that the process of oxygen evolution is due to the discharge of the ion common to both acid and alkaline solutions:

$$4 \, OH^- + 4 \, F = 2 \, H_2O + O_2.$$
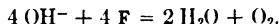
[1] Bennewitz, Z. phys. Ch. **72**, 216 (1910).
[2] Coehn and Osaka, Z. anorg. Ch. **34**, 86 (1903).

TABLE 27. POTENTIAL DIFFERENCE BETWEEN ANODE AND
SOLUTION WHEN OXYGEN FIRST APPEARS

METAL	OVERVOLTAGE	POTENTIAL vs. HYDROGEN
Gold	0.52	1.75
Platinum, smooth	0.44	1.67
Palladium	0.42	1.65
Cadmium	0.42	1.65
Silver	0.40	1.63
Lead	0.30	1.53
Copper	0.25	1.48
Iron	0.24	1.47
Platinized platinum	0.24	1.47
Cobalt	0.13	1.36
Nickel, smooth	0.12	1.35
Nickel, spongy	0.05	1.28

Current-density-voltage curves for iridium, platinum, and rhodium in 0.1-normal sulfuric acid are shown in Figure 38,[1]
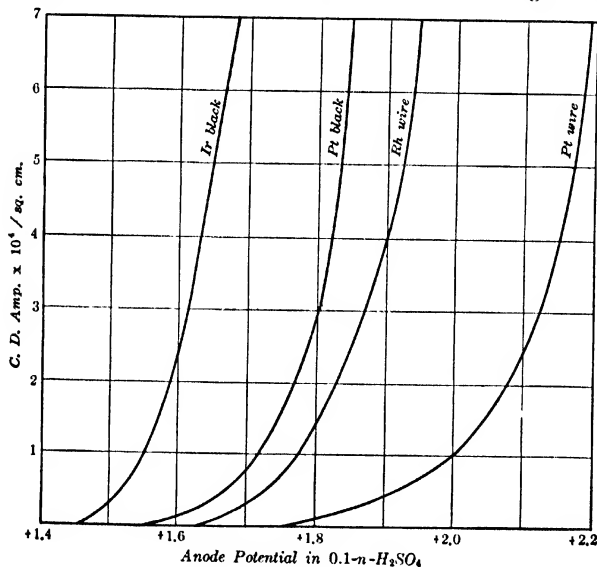
FIG. 38. — OXYGEN OVERVOLTAGE

[1] Westhaver, Z. phys. Ch. **51**, 65 (1905).
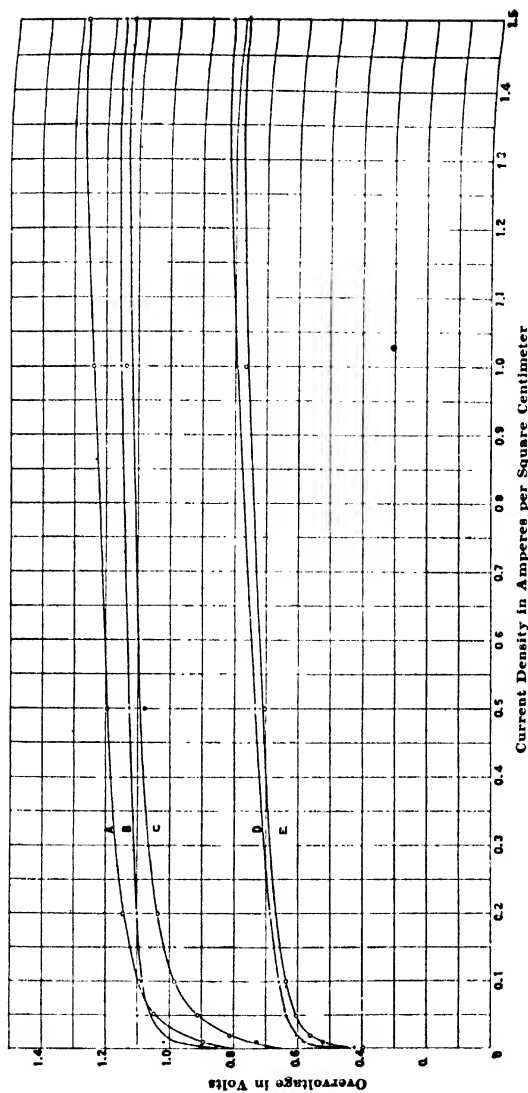
FIG. 39. — OXYGEN OVERVOLTAGE IN NORMAL KOH: A, GRAPHITE; B, CHEMMETAL; C, SILVER; D, COPPER; E, PLATINIZED PLATINUM

and overvoltage curves for graphite, chemmetal (Pb-Sn alloy) silver, copper, and platinized platinum in normal potassium hydrate in Figure 39.[1]

The electrode potentials of lead dioxide and smooth platinum polarized for two hours in normal sulfuric acid are nearly equal, as the following figures show:[2]

Amp /Sq Dm.	Potential Referred to Molal Hydrogen Electrode	
	Platinum	Lead Peroxide
0.4	+ 1.994	+ 1.982
2.3	+ 2.024	+ 2.061
4.6	+ 2.062	+ 2.126

In all cases the curves show much larger polarization for oxygen than for hydrogen, and the change of these values with time is also greater for oxygen,[3] and is accompanied by a surface change in the electrode. This overvoltage is reduced by increased temperature,[4] and by superimposing alternating current on direct.[5] With an alternating current relatively large compared with the direct current, oxygen can be liberated at an electrode potential less than its equilibrium potential. This takes place by the intermediate formation of hydrogen peroxide.

Oxygen polarization on smooth platinum electrodes depends on the previous history of the electrode and on the electrolyte. Even a little hydrofluoric acid added to sulfuric acid raises the electrode potential 0.1 volt.[6] The potential of platinum electrodes dipping in oxidizing solutions is altered by the illumination of the solution by ultra-violet light, as shown by Swensson.[7]

Oxygen overvoltage is explained in the same way as hydrogen overvoltage: by the formation of intermediate compounds. Oxygen forms oxides with the metal of the electrode, which have a higher free-energy content than gaseous oxygen, and therefore

[1] Knobel, Caplan, and Eiseman, Tr. Am. Electroch. Soc. **43**, 55 (1923).

[2] Mueller and Soller, Z. Elektroch. **11**, 865 (1905).

[3] Foerster and Piguet, Z. Elektroch. **10**, 714 (1904).

[4] Foerster, Z. phys. Ch. **69**, 259 (1909).

[5] Reitlinger, Z. Elektroch. **20**, 261 (1914); Grube and Dulk, Z. Elektroch. **24**, 237 (1918).

[6] Mueller, Z. Elektroch. **10**, 753 and 776 (1904); **11**, 866 (1905).

[7] Ark. f. Kem., Min. och Geol. Stockholm, **7**, 1 (1918-1919).

act as though the electrolytic solution pressure were increased. The oxide produced on platinized platinum, by whose intermediate formation oxygen is liberated, has been identified as PtO_3;[1] on nickel the peroxide NiO_2 is formed, which decomposes with the evolution of oxygen,[2] and an oxygen-evolving copper compound, probably an oxide higher than CuO is formed on electrolyzing copper anodes in 12-normal sodium hydrate, so that this may be considered general.[3]

Anodic Behavior of Pure Metals. — A metal used as anode can act in one of the following ways : (1) it may dissolve with 100 percent current efficiency, or (2) its solution may be accompanied by the discharge of anions, in which case the metal is only partly soluble, or (3) it may not dissolve at all.

(1) *Completely Soluble Anodes.* — A completely soluble anode does not dissolve at the equilibrium electrode potential, but always has concentration polarization and usually chemical polarization also. The anodic and cathodic polarizations are of about the
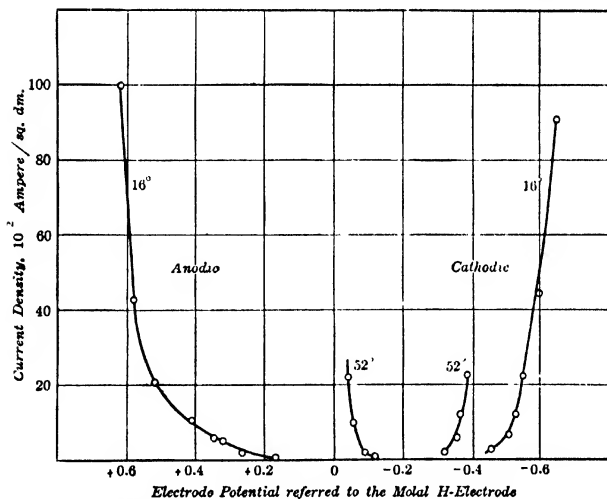
FIG. 40. — ANODIC AND CATHODIC OVERVOLTAGE OF NICKEL IN NORMAL
$NiCl_2$, 16° C.

[1] Grube, Z. Elektroch. **16**, 621 (1910).
[2] Foerster, Z. Elektroch. **13**, 414 (1907).
[3] Mueller and Spitzer, Z. Elektroch. **13**, 25 (1907).

same magnitude for any given metal, but the curves are not exactly the same shape, as shown for nickel in Figure 40.[1]

Though the current dissolves with 100 percent efficiency, all of the metal does not dissolve on account of the formation of a certain amount of *anode mud*, consisting of finely divided metal which separates from the anode and falls to the bottom of the cell. This is due to inhomogeneity of the metal, causing differences in the electrolytic solution pressure. The more negative parts dissolve, leaving the more positive parts behind, which become separated from the anode.

A question of great practical importance and of theoretical interest is the anodic behavior of metals of more than one valence. The discussion will be confined to two valences. Whether the metal goes into solution with the higher valence or with the lower is determined by the values of the corresponding electrode potentials, and the concentrations of the two kinds of ions formed. There are two cases to be considered: (1) Suppose the electrode

potential
$$\mathbf{E_1} = \frac{RT}{l\mathbf{F}} \log \frac{P}{p_{M^{l+}}}$$

for the reaction $M + l\mathbf{F} = M^{l+}$ (3)

is more negative than $\mathbf{E_2} = \dfrac{RT}{h\mathbf{F}} \log \dfrac{P}{p_{M^{h+}}}$

for the reaction $M + h\mathbf{F} = M^{h+}$, (4)

where l is the lower number of valences and h is the higher. ($\mathbf{E_3}$ corresponds to the reaction $M^l + (h - l)\mathbf{F} = M^{h+}$.) Then if the solution contains at first no ions of the metal but only a salt with whose anion the metal can form a simple salt, the metal will go into solution only in the lower state of oxidation. In any given solution the concentrations of the ions M^{l+} and M^{h+} must adjust themselves to such values that $\mathbf{E_1} = \mathbf{E_2} = \mathbf{E_3}$. As M^{l+} increases in concentration due to continued electrolysis, M^{h+} must also increase correspondingly, and if $\mathbf{E_1^\circ}$ and $\mathbf{E_2^\circ}$ are not too far apart it is possible that for high concentrations of M^{l+} the concentration of M^{h+} may be appreciable. In this solution the metal would then dissolve with a valence lying between h and l.

If an excess of M^{h+} were added to the solution, the value of $\mathbf{E_2}$ would momentarily be less negative than that of $\mathbf{E_1}$. Therefore the reaction (3) corresponding to $\mathbf{E_1}$ would take place and drive the reaction (4), corresponding to $\mathbf{E_2}$, in the reverse direction, until

[1] Schweitzer, Z. Elektroch. **15**, 607 (1910); see also Schoch, Am. Ch. J. **41**, 240 (1909).

the two values of E_1 and E_2 again become equal.   This is analogous to what takes place on dipping a zinc rod in a copper sulfate solution, the electrode potential of $Zn|Zn^{++}$ corresponding to E_1 and $Cu|Cu^{++}$ to E_2.   Zinc dissolves and precipitates copper until the two electrode potentials are equal.   The reactions are placed side by side for comparison.

$$
\begin{array}{ll|l}
hM + hl\mathbf{F} = hM^{l+} \text{ cor. to } E_1 & & Zn + 2\,\mathbf{F} = Zn^{++} \\
\underline{lM^{h+} - hl\mathbf{F} = lM,} \text{ cor. to } E_2 & & \underline{Cu^{++} - 2\,\mathbf{F} = Cu} \\
(h - l)M + lM^{h+} = hM^{l+} & (5) & Zn + Cu^{++} = Zn^{++} + Cu
\end{array}
$$
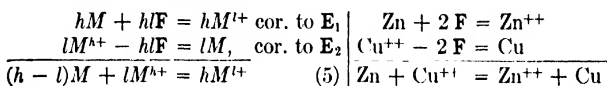
The addition of M^{h+} ions would also have the effect of making E_3 less negative, and the same result would be reached by using the corresponding reaction:

$$
\begin{array}{ll}
(h - l)M + l(h - l)\mathbf{F} = (h - l)M^{l+} & \text{corresponding to } E_1 \\
\underline{lM^{h+} - l(h - l)\mathbf{F} = lM^{l+}} & \text{corresponding to } E_3 \\
(h - l)M + lM^{h+} = hM^{l+} & \qquad\qquad (5)
\end{array}
$$
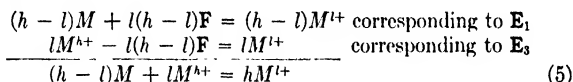
Or the reaction corresponding to E_2 can be considered to drive that corresponding to E_3 in the reverse direction, with the same result. Doubtless all take place simultaneously.   Iron, in chloride or sulfate solutions, belongs to this class, as shown by the values of E_1° and E_2° in Table 21, page 87.   Similarly for tin [1] in chlorides and sulfates, lead in hydrochloric acid, hydrofluosilicic acid, and sodium hydrate, and bismuth and antimony in chloride solutions.[2]

Mercury is an exceptional metal in that the equilibrium ratio of M^{l+}/M^{h+} is not exceedingly large as in the cases mentioned above, but[3] $Hg_2^{++}/Hg^{++} = 120$.   Therefore in a solution in which this equilibrium has been reached one mercuric ion dissolves for every 120 mercurous ions.

(2) When E_2° is more negative than E_1°, the metal goes into solution principally in the higher valence, but as explained above, if E_1° and E_2° are not too far apart, with higher concentrations of M^{h+} appreciable quantities of M^{l+} may dissolve, but the ratio of the concentrations must stay such as to make the three electrode potentials equal, including E_3.   If an excess of M^{l+} ions were added to the solution, E_1 would become less negative than E_2, and the reaction corresponding to E_2 would proceed and drive that corre-

[1] Elbs and Thuemmel, Z. Elektroch. **10**, 364 (1904).   See also Wohlwill, *ibid.* **9**, 635 (1903).

[2] Elbs and Nuebling, Z. Elektroch. **9**, 781 (1903); Elbs and Foerssell, Z. Elektroch. **8**, 780 (1902).

[3] Ogg, Z. phys. Ch. **27**, 285 (1898).

sponding to E_l in the reverse direction until the two electrode potentials again become equal. The reactions are:

$$hM^{l+} - lh\mathbf{F} = hM \qquad \text{corresponding to } \mathbf{E_1}$$
$$\underline{lM + lh\mathbf{F} = lM^{h+}} \qquad \text{corresponding to } \mathbf{E_2}$$
$$hM^{l+} = (h - l)M + lM^{h+} \qquad (6)$$
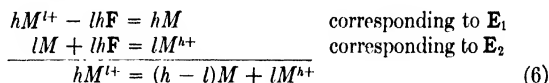
As before, the other reactions give the same result. This is responsible for part of the copper content of the anode mud in copper refining. The solution at the anode becomes more concentrated in cupric ions and consequently more so in cuprous ions than the body of the solution. As soon as this becomes a little diluted by circulation at a short distance from the anode, cuprous ions must react according to (6):

$$2\,Cu^+ = Cu + Cu^{++}, \qquad (7)$$
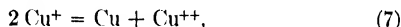
since on dilution the value of the mass action constant, $Cu^{++}/(Cu^+)^2$ will not remain constant without the removal of some cuprous ions, since this concentration is squared.

Gold acts in the same way as copper and finely divided gold is separated at the anode.

Silver exists as the ions Ag^+ and Ag_2^+, which act in the same way as the two copper ions.[1] It is therefore important in using the silver coulometer to prevent the metallic silver from dropping on the cathode and also to keep the anode liquid from the cathode so no Ag_2^+ ions can be deposited.

If the solution contains an anion with which the metal of the anode can form a complex, the behavior of the metal may be changed. If, for example, the ion M^{h+} has a much stronger tendency to form complexes than M^{l+}, its concentration would be so far reduced that $\mathbf{E_2}$ becomes more negative than $\mathbf{E_1}$, though the molal electrode potentials are just the reverse, and case (1) would change into case (2). On the other hand, if M^{l+} has a much greater tendency to form complexes than M^{h+}, case (2) would be changed into case (1). In general metal ions in a high state of oxidation show a greater tendency to form complex salts than ions of the same metal in a lower state of oxidation. Copper and gold are exceptions to this rule; cuprous and aurous ions have a greater tendency to form complexes than cupric and auric. Therefore copper dissolves in cyanide solutions as cuprous copper, because the concentration of cuprous ions is so reduced by entering the

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[1] Richards and Heimrod, Z. phys. Ch. **41**, 302 (1902).

complex that the electrode potential corresponding to Cu + **F** = Cu⁺ has been made more negative than that corresponding to Cu + 2 **F** = Cu⁺⁺.

Anodic Behavior of Alloys. — Alloys can exist in three conditions: (a) as a mechanical mixture, when the metals do not dissolve each other or form any compounds. In this case, an example of which is tin-bismuth alloys shown in Figure 41, the alloy has the same electrode potential as the pure more negative
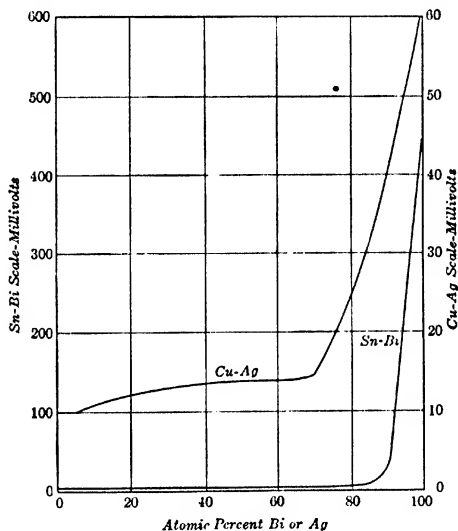
FIG. 41. — ELECTRODE POTENTIALS OF ALLOYS: E.M.F.'s OF THE CELLS: S_N | n-H$_2$SO$_4$ | S_NBi$_x$ AND Cu | n-CuSO$_4$ | CuAg$_x$.

metal, except for compositions in which there is very little of the negative component. Thus the figure shows the electrode potential of SnBi$_x$ is the same as that of the more electronegative metal, tin, until the alloy contains 80 percent of bismuth.

If bismuth ions are added to the solution in which a tin-bismuth alloy dips, tin will go in solution and deposit bismuth ions until their concentration is reduced to the point at which the electrode potential of bismuth equals that of tin for this solution. When this alloy is electrolyzed as an anode, practically only tin goes in

solution with only enough bismuth to keep the electrode potential of bismuth equal to that of tin, and this amount is negligible. With 90 percent bismuth the alloy begins to have a less negative *electrode potential and for very small amounts of tin the electrode potential becomes equal to that of bismuth.*

(b) The metals form a solution. In this case there must be a loss of free energy and the components have smaller electrolytic solution pressures than when in the pure state. As the composition is varied, the electrode potential changes from that of one pure
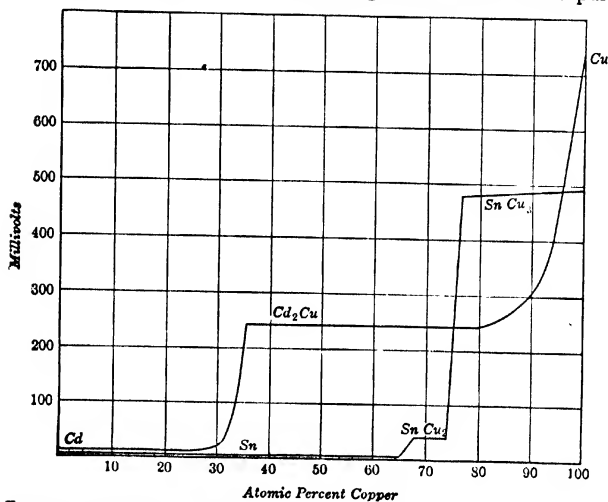
Fig. 42. — ELECTRODE POTENTIALS OF ALLOYS: E.M.F.'s OF THE CELLS: Cd | n-CdSO₄ | CdCuₓ AND Sn | n-H₂SO₄ | SnCuₓ

metal to that of the other without any break in the curve, as represented in the curve for copper-silver alloys.[1]

Anodic corrosion takes place as in the first case: the electrode potential of the metal alloy must be the same referred to each kind of ion present, but these are less than for the pure metals.

(c) The metals form definite chemical compounds, which have their own electrolytic solution pressures. On going into solution they split up into the ions of each metal, and by the mass action law the potential of the compound depends on the product of the

[1] Herschkowitsch, Z. phys. Ch. **27**, 123 (1898).

ion concentrations of the metals. This case is illustrated by the diagrams of the electrode potentials of tin-copper and cadmium-copper alloys, in Figure 42.[1] Up to 65 atomic percent copper the *electrode potential of the tin-copper alloy is the same as that of pure tin, but at this point a different potential corresponding to* $SnCu_2$ *occurs. At 75 atomic percent copper the potential changes to a new value corresponding to* $SnCu_3$. Since compounds go into solution as such and dissociate only afterwards, it would evidently be impossible to separate two such metals at the anode.

In the copper-cadmium curve the horizontal line represents the electrode potential of the compound Cd_2Cu, and the two sloping curves are due to solid solutions of cadmium with Cd_2Cu and of Cd_2Cu with copper. Many similar cases have been investigated.[2]

In the anodic solution of any alloy the general principal is that the most negative metal or compound that is at the surface exposed to the action of the current dissolves first. If this is all used up and the current does not have further access to underlying portions because they are covered by the other components, the next most negative compound or metal will dissolve, at an electrode potential corresponding to the new process. In this process the current may eat away the more negative metal from the neighborhood of the more positive metal or compound and so loosen it that it becomes detached and goes into the anode mud. This is illustrated by zinc containing impurities,[3] and by the corrosion of brasses.[4] If the copper content of brasses is greater than 50, in general electrolytic corrosion results in the formation of a corrosion product of the same composition as the anode, because the copper has to be removed so the current can attack the zinc, but the corrosion product of low-copper brass is pure zinc, because there is not enough copper to keep the current from the zinc. In sulfate solutions, however, the corrosion is constant for all compositions, for a reason that is not clear.

In general the corrosion of alloys is different for different solutions. Thus while both copper and tin dissolve with 100 percent current efficiency in sodium chloride solutions, and copper-tin alloys as well in which the copper content is more than 75 or less than 35 percent, other compositions dissolve scarcely at all in sulfate solutions, but all compositions dissolve in alkaline tartrate

[1] Puschin, Z. anorg. Ch. **56**, 1 (1907).
[2] Kremann, Z. Metall. **12** (1920) and **13** (1921).
[3] Mylius and Fromm, Z. anorg. Ch. **9**, 162 (1895).
[4] Lincoln, Klein, and Howe, J. Phys. Ch. **11**, 501 (1907).

and acid oxalate solutions. This is probably due to the more negative potential of copper on account of the formation of complex salts in these solutions, while the non-corrosion in sulfates is due to a protecting film of stannic oxide.[1]

In general changes in the rate of corrosion occur only on the appearance or disappearance of a phase as shown in the equilibrium diagram.[2]

Insoluble and Partly Soluble Anodes. — If there is some resistance to the formation of ions by an anode, so great that metal ions are formed with less than 100 percent current efficiency or not at all, the metal is said to be *passive.* This may be (1) *mechanical* passivity, due to some kind of insoluble layer formed over the surface of the anode, protecting the underlying metal from the current, or (2) *chemical* passivity, where no such layer can be detected.

Mechanical passivity may be due to the deposition of some colloid on the anode, but it is more generally due to the formation of an insoluble compound from the metal of the anode and an anion of the solution. This layer is usually porous and therefore has the effect of increasing the current density, if the current is held constant. This means a higher electrode potential and the possibility of some new electrode process such as the oxidation of the metal to a higher state or the deposition of anions.

A lead anode in a sulfate solution is an example of mechanical passivity. If the impressed voltage is great enough, in a very short time the surface is covered with lead peroxide. This is due to the formation of nonconducting, porous lead sulfate which insulates part of the surface, increases the current density, and therefore raises the electrode potential to a value which oxidizes bivalent lead ions to quadrivalent, giving lead persulfate. This hydrolyzes rapidly and deposits lead peroxide in a continuous, protecting layer:[3]

$$Pb(SO_4)_2 + 2\,H_2O = PbO_2 + 2\,H_2SO.$$
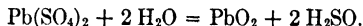
Since lead dioxide is a conductor, further electrolysis merely liberates oxygen, by the deposition of sulfate and hydroxyl ions. If the voltage is not allowed to rise to the point at which lead dioxide is formed, lead remains active and forms sulfate. A patent by Pollak for the formation of storage-battery plates is

[1] Curry, J. Phys. Ch. **10**, 474 (1906).
[2] Rowland, J. Phys. Ch. **12**, 180 (1908).
[3] Elbs and Fischer, Z. Elektroch. **7**, 343 (1900); Elbs and Nuebling, Z. Elektroch. **9**, 776 (1903).

based on this fact.[1] A lead plate also stays active if the sulfuric acid has a greater specific gravity than 1.65, for in this case lead persulfate is stable and soluble and no protecting layer is formed on the surface.

Still another method of keeping the surface of a lead anode active is to add some salt to sulfuric acid that forms a soluble compound with lead. Some of the lead ions combine with the anions with which it forms the soluble salt and come in contact with sulfate ions at a certain distance from the electrode, with the result that the sulfate either adheres more loosely or falls off altogether. Whether the sulfate sticks to the anode or is separated from it depends on the concentration of the solution both as regards the relative amounts of the two salts and their total amounts. If a small amount of the anions are present that form a soluble salt with lead, the process is suitable for forming storage-battery plates, while if the proportion is large, insoluble products are made according to the Luckow process.[2]

Thallium acts like lead in sulfuric acid.[3]

The hydrates of many metals are insoluble, and consequently these metals show mechanical passivity in hydrate solutions. Thallium, for example, dissolves in the univalent state in 0.1-normal sodium hydrate at current densities below 0.35 amp./sq. cm., but if the current density is increased, these ions are formed so rapidly that the solution becomes supersaturated and they precipitate as oxide on the anode. This causes a further rise in voltage and the consequent evolution of oxygen.[3]

As a final example may be mentioned that gold anodes are covered with a protecting layer of insoluble sodium gold cyanide when electrolyzed in sodium cyanide, but potassium gold cyanide is soluble and does not produce the passive state.[1]

For many metals, including tantalum, columbium, aluminum, magnesium, cadmium, zinc, bismuth, copper, and tin, these protecting films take on the peculiar property of allowing only very small currents to pass when used as anodes, but much larger currents when used as cathodes. This was first noticed by Buff[5] for aluminum in sulfuric acid and sulfates. Graetz[6] showed

[1] See Morse, *Storage Batteries*, p. 188 (1912).

[2] Germ. Pat. No. 91, 707 (1894); Le Blanc and Bindschedler, Z. Elektroch. **8**, 255 (1902); Schleicher, Z. Elektroch. **17**, 554 (1911).

[3] W. J. Mueller, Z. Elektroch. **15**, 696 (1909).

[4] Coehn and Jacobsen, Z. anorg. Ch. **55**, 321 (1907).

[5] Lieb. Ann. **102**, 269 (1857).

[6] Ann. d. Phys. **62**, 323 (1897).

this property could be used for rectifying alternating currents. *This is therefore called the rectifying action or the valve action of electrodes.* The connections for utilizing both positive and nega-

tive waves of alternating currents are shown in Figure 43. There are four cells with one aluminum electrode and one of carbon, iron, or platinum. Since aluminum allows the passage of appreciable currents only as cathode, it can be easily verified that the current in OP is in the direction of the arrow whichever way it flows through the alternator.
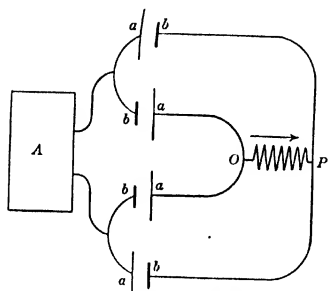
FIG. 43. — ELECTROLYTIC RECTIFIER. A, ALTERNATING CURRENT SOURCE, a, ALUMINUM ELECTRODES; b, CARBON ELECTRODES, OP, EXTERNAL CIRCUIT

The formation of a layer of this kind may be represented by a curve showing the increase in voltage with the time during which a constant current passes the electrode. If a tantalum electrode, which shows valve action in nearly all electrolytes, is electrolyzed with a constant current density of a few tenths of an ampere per square decimeter in a 0.05-normal acid or alkali solution, the voltage rises as shown in Figure 44.[1] This curve consists of three parts, marked a, b, and c. At the point joining a and b small sparks begin to pass and the rate of voltage rise becomes less. Finally a critical or maximum voltage is reached when large sparks pass between the electrode and solution and no further rise in voltage takes place. For tantalum in dilute alkali carbonate this is about 1000 volts.[2] The voltage at which the first sparking point occurs depends on the metal, and the second on the electrolyte.[3] During the formation of the protecting layer only about 5 percent of the current is used to form, while 95 percent evolves oxygen, even on an aluminum electrode which has a great affinity for oxygen. This is supposed to be due to a film of oxygen gas across which the electrons from oxygen ions pass, so that atomic or nascent oxygen does not come in contact with aluminum.

[1] Schulze, Ann. d. Phys. **34**, 657 (1911).
[2] Schulze, Ann. d. Phys. **23**, 246 (1907).
[3] Schulze, Ann. d. Phys. **34**, 708 (1911).

If the metal is one for which the critical voltage is about 200 volts, the part b of the curve disappears, as in curve I, and in some cases b goes over into c without a sharp break, as in III.   These curves are raised only slightly by increasing the current density.[1]   High temperature tends to destroy the valve action of these films.[2]
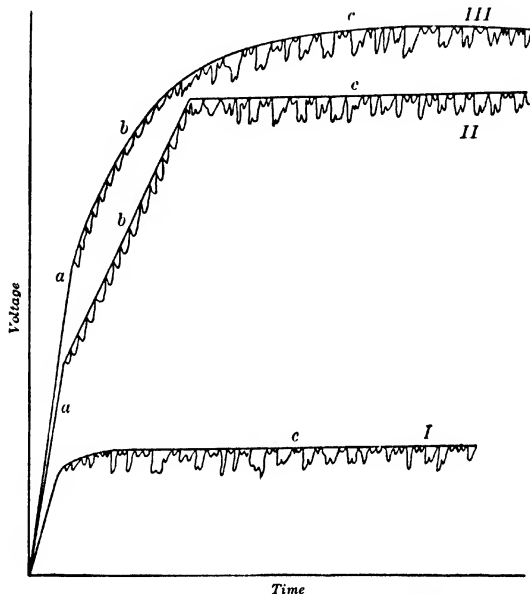
Fig. 44. — Valve Action of Tantalum

According to determinations based on light interference the maximum thickness of film formed on aluminum is between 5×10^{-4} and 5×10^{-5} millimeters.[3] This thickness can, however, be increased indefinitely by continued electrolysis with the voltage below the critical voltage.   A small current flows which slowly builds up the layer.   By dissolving out the aluminum metal the layer can be obtained alone and its dielectric strength measured after drying, and the thickness can be calculated from

[1] Schulze, Ann. d. Phys. **21**, 929 (1906).
[2] Fischer, Z. Elektroch. **10**, 869 (1904).
[3] Zimmerman, Tr. Am. Electroch. Soc. **5**, 147 (1904).

this. In phosphoric acid aluminum electrolyzed with a current density of 0.5 amp./sq. dm. for 25 minutes gave a film $2.7 \cdot 10^{-5}$ cm. thick; in 2.8 hours it was $830 \cdot 10^{-5}$ cm.[1]

In chemical composition a rectifying film is always the oxide of the metal of the electrode in the layer next the electrode; outside this layer it is the metal combined with the anion of the solute.[2] The oxide portion of the film holds a thin film of oxygen gas which is responsible for the rectifying action. This was shown by placing a formed electrode under an air pump and evacuating, whereupon a stream of minute bubbles escaped from the electrode. After this the resistance as anode was at first quite low, but rapidly increased to its initial value.[3]

When a formed electrode is used as cathode there is also a minimum potential difference at which a current will pass, which depends on the metal, the thickness of film, and the electrolyte.[4] Thus the minimum voltage of tantalum as cathode is 1.51 times that of aluminum formed at the same voltage. If the ion concentration is halved, the minimum voltage increases about 7 percent. For tantalum formed at 85 volts the minimum cathode voltage for alkali cations is 10 volts, for hydrogen ions, 46.3 volts. The film therefore acts in the same way for a cathode as for an anode, and differs only in degree in the two cases.

This applies only to metals whose oxides are not reduced to the metallic state at the cathode, such as tantalum, aluminum, and magnesium. The film is destroyed when the electrode is cathode for such metals as cadmium, zinc, antimony, and bismuth.

The present theory why some protecting films have a valve action and others do not is that in rectifying films the solid part holds a thin layer of oxygen close to the surface of the electrode and that this oxygen layer is responsible for the rectifying action. There is no explanation, however, why some solid protecting layers produced by electrolysis allow the formation of an oxygen film with this property, and why others do not. There is also no good explanation why the current flows more easily in one direction across the oxygen film than in the other. It has been suggested that the reason is that metals give up electrons more easily than anions, but decomposition points show that this is not so.[5]

[1] Schulze, Ann. d. Phys. **21**, 929 (1906).
[2] Schulze, Ann. d. Phys. **24**, 43 (1907).
[3] Guthe, Phys. Rev. **15**, 327 (1902).
[4] Schulze, Ann. d. Phys. **41**, 593 (1913).
[5] Schulze, Z. Elektroch. **20**, 592 (1914) and following discussion.

According to Guthe [1] the film is a kind of semipermeable membrane allowing the passage of some kinds of ions but not of others. This is not in agreement with the fact that a minimum voltage is required to pass an appreciable current even when the film is on the cathode, but it is suggestive that Guthe found unidirectional conductance with a semipermeable membrane made from copper sulfate and potassium ferrocyanide. In the cell

$$Cu|CuSO_4|K_4Fe(CN)_6|Pt$$

this membrane has a high resistance for the passage of the current from copper sulfate to cyanide, but hardly any in the opposite direction.

Protecting layers of oxygen can be produced in the absence of a solid protecting layer at high current densities. If a short platinum wire is electrolyzed at a high current density as anode in sulfuric acid with a large lead cathode, the current is practically broken when the protecting layer of oxygen is formed. As there is nothing to hold it on the surface of the platinum wire, the current starts again, and this takes place with great rapidity. This is the Wehnelt interruptor sometimes used for induction coils. It does not work if the platinum wire is used as cathode, or without inductance in the circuit. [2]

Aluminum also shows rectifying action in fused salts, among which are nitrates, hydroxides, chlorates, and bichromates. The efficiency is said to be 60 to 80 percent. [3]

Chemical Passivity. — The chemically passive state was first observed by Keir [4] who found that if a solution of silver in pure colorless nitric acid were poured on a piece of clean iron wire at first a precipitation of silver took place, but the action of iron on the liquid soon ceased and the silver redissolved. Schönbein [5] showed that this state, which he called passive, could be produced by electrolyzing iron as anode in solutions of oxygen acids.

It has been shown above that nearly all metals depart considerably from their equilibrium electrode potentials when polarized anodically, though the anode still dissolves with 100 percent current efficiency. If the electrode potential increases to such an extent that discharge of anions partly replaces solution of metal, or if the metal dissolves with a higher valence than corresponds

[1] Guthe, Phys. Rev. **15**, 327 (1902).
[2] Wehnelt, Wild. Ann. **68**, 233 (1899).
[3] Hambuechen, U. S. Pat. 732, 631 (1903).
[4] Phil. Trans. **80**, 359 (1790).
[5] Phil. Mag. **9**, 53 (1836).

to its most negative equilibrium electrode potential, the metal is said to be passive. Passivity may therefore be considered an extreme case of polarization.

Table 28 shows how chemical passivity manifests itself,[1] with a gradually increasing and then a gradually decreasing applied voltage.

TABLE 28.   NICKEL WIRE OF 0.14 SQ.CM. SURFACE IN NORMAL H_2SO_4

IMPRESSED VOLTAGE	TIME	CURRENT AMP. $\times 10^6$	ELECTRODE POTENTIAL OF ANODE REFERRED TO HYDROGEN
0.0	0,0	——	− 0.070
0.2	2	480	+ 0.244
0.3	4	750	+ 0.260
0.4	6	1350	+ 0.290
0.5	8	3800	+ 0.326
0.6	10	7200	+ 0.376
0.7	11	13	——
0.7	12	6	+ 1.225
0.4	18	1.5	+ 0.960
0.16	26	0.1	+ 0.735
0.08	34	0.07	+ 0.666
0.01	50	0.04	+ 0.590
Open	55	——	− 0.100

It is seen that as the applied voltage increases the current increases for ten minutes and then suddenly drops, while the electrode potential simultaneously becomes much more positive. When the impressed voltage is reduced, in this experiment the current remained at a low value, but these results are not exactly reproducible, and in other similar runs the current gradually increased when the impressed voltage was low. Up to the point where the sudden drop in current takes place nickel ions go into solution; but at this point the nickel electrode becomes charged with oxygen and further increase in voltage would result chiefly in the liberation of oxygen. When the circuit is opened nickel gradually resumes the active state.

In nickel chloride solutions nickel remains active under conditions which would cause passivity in nickel sulfate. This shows that anions have a determining influence on the appearance of passivity of nickel; the halogens oppose it, while oxidizing anions, including chromates, nitrates, and hydroxyl ions, cause passivity to

[1] Fredenhagen, Z. phys. Ch. **63**, 32 (1908).

appear. The only cation that has any effect on the passivity of nickel is hydrogen, and this tends to prevent it. Nickel dissolves quantitatively in normal sulfuric acid at a current density of one ampere per square decimeter, while in other sulfates it does not dissolve at half this current density.[1]

Increased temperature tends in all cases to remove passivity.

Iron behaves very much the same as nickel. Under certain conditions iron electrodes can be gotten into an unstable state in which they change back and forth from active to passive iron at a uniform rate. A cell made from two such electrodes placed in a solution of bichromate and sulfuric acid will give an alternating current if one is active at the time the other is passive.[2]

Finely divided iron made active by polarizing cathodically in potassium hydrate remains active as anode in this solution, and changes to ferrous hydroxide when a current passes. Finely divided iron is the active material of the negative plate of the Edison accumulator.

Cobalt can be made passive in solutions of certain alkali salts.[3]

Chromium exists in the bivalent and trivalent states in chromium salts and in the hexavalent state in chromates. If chromium is polarized as anode in dilute solutions, nearly all dissolves in the hexavalent state and then reacts with hydroxyl ions according to the equation,

$$Cr^{6+} + 8\,OH^- = CrO_4^{--} + 4\,H_2O.$$
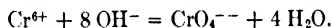
A piece of chromium made passive by anodic polarization is unattackable by cold acids and gives no potential against platinum when the two are placed in chromic acid.[4] If the temperature is raised to near the boiling point, the velocity of formation of bivalent ions is increased so that nearly all dissolves as Cr^{++} ions and the metal is now active.

Some samples of chromium show a periodic change from the passive to the active state both as to the velocity of chemical solution in acid [5] and the electrode potential.[6] The cause of this is not understood. An alternating current cell can also be

[1] Le Blanc and Levi, Boltzmann Festschrift, p. 187 (1904).

[2] Kistiakowsky, Nernst Festschrift, p. 224 (1912); Z. Elektroch. **15**, 268 (1909).

[3] Byers, J. Am. Ch. Soc. **30**, 1718 (1908).

[4] Hittorf, Z. Elektroch. **4**, 482 (1898); **6**, 6(1899); **7**, 168 (1900); Kuessner, Z. Elektroch. **16**, 767 (1910).

[5] Ostwald, Z. phys. Ch. **35**, 33 and 204 (1900).

[6] Brauer, Z. phys. Ch. **38**, 441 (1901).

made with chromium electrodes, but the voltage change is not as great as with the iron-electrode cell mentioned above.[1]

If manganese is polarized anodically with 5 amperes per square decimeter in half-normal sulfuric acid, it goes into solution as bivalent ions, and the electrode potential changes in 218 minutes from -0.6 to -0.3 volt. At the same time both hydrogen and oxygen are given off, which is explained by assuming that some manganese dissolves as univalent and as trivalent ions, which then react as follows:[2]

$$Mn^+ + H^+ = Mn^{++} + \tfrac{1}{2} H_2,$$
$$2Mn^{+++} + 2\,OH^- = 2\,Mn^{++} + H_2O + \tfrac{1}{2}\,O_2.$$
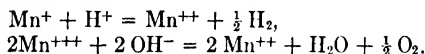
In alkaline solutions manganese becomes passive and goes into solution with seven valences and then reacts with hydroxyl ions:[3]

$$Mn^{7+} + 8\,OH^- = MnO_4^- + 4\,H_2O.$$
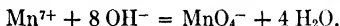
Platinum shows the most marked case of passivity. It is so strongly passive that it was for a time supposed not to be capable of sending ions into solution. But even platinum anodes dissolve to a slight extent. This anodic solution is much increased by superimposing an alternating current on the direct.[4]

Gold anodes are passive in a solution of $HAuCl_4$ and chlorine is liberated on them as on platinum. The addition of hydrochloric acid or increased temperature removes the passive state.[5]

The explanation of chemical passivity now most generally accepted is that it is due to a retardation of the velocity of that electrode reaction which takes place with the greatest free-energy decrease, and this retardation is due to the negative catalytic effect of the solid solution of an oxide of the anode metal on the surface of the anode.[6] This is somewhat similar to Faraday's original explanation that passivity is due to a film of oxide, but accounts for the fact that no film can be detected.

Discharge of Halogen Ions. — Fluorine decomposes water with the evolution of oxygen and ozone and cannot be obtained by electrolyzing aqueous solutions.

[1] Kistiakowsky, Nernst Festschrift, p. 224 (1912); Z. Electroch. **15**, 268 (1909).

[2] Kuessner, Z. Elektroch. **16**, 758 (1910).

[3] Lorenz, Z. anorg. Ch. **12**, 393 (1896).

[4] Margules, Ann. Phys. **65**, 629; **66**, 540 (1898); Ruer, Z. Elektroch. **9**, 235 (1903); **11**, 661 (1905).

[5] Wohlwill, Z. Elektroch. **4**, 381 (1898).

[6] Le Blanc, *Lehrbuch der Elektrochemie*, 3d ed., p. 237 (1903); Schoch, J. Phys. Ch. **14**, 719 (1910); Foerster, *Elektrochemie wässeriger Lösungen*, p. 429 (1922).
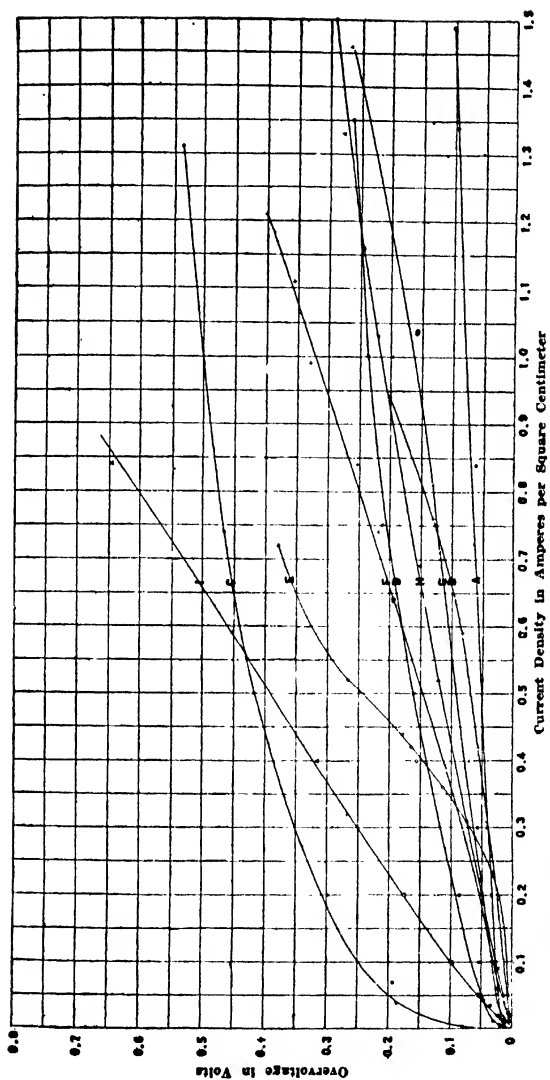
FIG. 45. — HALOGEN OVERVOLTAGES: A, Cl_4 ON PLATINIZED PLATINUM; B, Cl_4 ON SMOOTH PLATINUM; C, Cl_4 ON GRAPHITE; D, Br_2 ON PLATINIZED PLATINUM; H, I_2 ON SMOOTH PLATINUM; I, I_1 ON GRAPHITE. SATURATED SOLUTIONS OF THE SODIUM OR POTASSIUM HALIDE, ALSO SATURATED WITH THE HALIDE, USED

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The halogen overvoltages for different anodes are shown in Figure 45.[1]

Decomposition of Points. — If a gradually increasing voltage is applied to an unattackable electrode placed in a solution of an electrolyte, only a very small residual current flows until a certain value of the impressed voltage is reached. At this point the current begins to increase rapidly. This is called the decomposition point and its value is usually determined by making a graph of the impressed voltages and the corresponding currents. Le Blanc was the first to determine decomposition points. Some of his results are given in Table 29.[2]

TABLE 29.   DECOMPOSITION POINTS

SALT	VOLTS	SALT	VOLTS
$ZnSO_4$	2.35	$Cd(NO_3)_2$	1.98
$ZnBr_2$	1.80	$CdSO_4$	2.03
$NiSO_4$	2.09	$CdCl_2$	1.88
$NiCl_2$	1.85	$CoSO_4$	1.92
$Pb(NO_3)_2$	1.52	$CoCl_2$	1.78
$AgNO_3$	0.70	H_2SO_4	1.67

According to Westhaver,[3] decomposition points determined in this way are inaccurate because they depend on the sensitiveness of the galvanometer and the scale on which the results are graphed, but this inaccuracy disappears if the logarithms of the current densities are used in place of the current densities themselves.

Le Blanc also found that for many metals, at the decomposition point the electrode potential of the indifferent electrode is the same as that which the metal would show if placed in the solution in question.[4] This applies only to the small currents used in decomposition point as is evident from what has preceded on the cathodic polarization of metals.

In carrying out an electrolysis it is always necessary to use a higher voltage than the decomposition voltage because of the ohmic resistance of the cell and on account of the increase in polarization with the current density. The ratio of the de-

[1] Knobel, Caplan, and Eiseman, Tr. Am. Electroch. Soc. **43**, 55 (1923).
[2] Z. phys. Ch. **8**, 299 (1891).
[3] Z. phys. Ch. **51**, 65 (1905).
[4] Z. phys. Ch. **12**, 333 (1893).

composition voltage to the voltage required to give a current density high enough for practical work is the *voltage efficiency*, and the product of this and the current efficiency is the *energy efficiency*.

ELECTROLYTIC REDUCTION

Every reaction taking place at a cathode is a reduction and every reaction at an anode is an oxidation, and in any electrolytic cell the two must be equivalent. In spite of the fact that all electrochemical reactions are oxidations or reductions, it is convenient to confine the terms *oxidation* and *reduction* to those cases where the products at anode and cathode are kept separate or where the desired product is made at only one electrode.

If an oxidation does not take place with 100 percent current efficiency, oxygen is evolved, and hydrogen is evolved if a reduction falls short of the theoretical. This gives a convenient method of following the current efficiency of these reactions by comparing the amount of hydrogen or oxygen given off by the experimental cell with that from a water coulometer during the same time. This gives the efficiency at the time of collecting the gas, and not the average efficiency which would be obtained by analyzing samples of the solution taken from time to time.

Reduction may consist in (1) removing positive charges from ions, such as

$$Fe^{+++} = Fe^{++} + F \text{ or } Fe^{+++} + H \text{ (nascent)} = Fe^{++} + H^+;$$
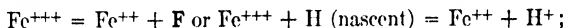
(2) adding negative charges:

$$Cl_2 - 2F = 2Cl^- \text{ or } Cl_2 + 2H = 2Cl^- + 2H^+;$$

(3) adding hydrogen;

$$C_2H_2 + 2H = C_2H_4,$$
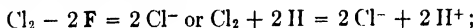
in 65 percent sulfuric acid at $100°$ C.;[1] (4) removing oxygen:

$$NaClO + 2H = NaCl + H_2O.$$
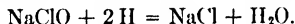
Both of the reactions given under (1) and under (2) probably take place at the same time, but all electrochemical reductions may be considered due to primarily deposited hydrogen. If the substance to be reduced depolarizes rapidly, the concentration of hydrogen on the cathode will remain below atmospheric pressure and reduction would then take place at an electrode potential which is more positive than that of a hydrogen electrode surrounded

[1] U. S. Pat. 711, 565 (1902).

by hydrogen at atmospheric pressure in the same solution. In this case the current efficiency will be close to 100 percent. If the depolarizer does not act rapidly, the hydrogen concentration on the cathode may increase to atmospheric pressure and partly escape from the cell, and the current efficiency may fall to zero.

Both reductions due to change of charge and those in which hydrogen enters the reaction permanently are subject to chemical polarization or overvoltage. Though ferric iron is reduced to ferrous and ferrous is oxidized to ferric in simple salts with polarization due principally to concentration,[1] this is not true of many other similar reactions, including the reduction of hydrochloric acid solutions of molybdic acid to Mo^{+++} salts, of Cb^{5+} to Cb^{3+}, sulfuric acid solutions of titanic acid to Ti^{3+}, and hydrochloric acid solutions of stannic to stannous salts.[2] The explanation of this may be that ions with high valences are at high dilution, are soon used up, and are not readily produced from complex ions.

An example of polarization where hydrogen is taken up by the oxidizing agent is a solution of chinon and hydrochinon, between which the following reversible reaction applies:

$$C_6H_4O_2 + 2 H \rightleftharpoons C_6H_4(OH)_2.$$
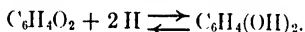
A mixture of chinon and hydrochinon gives a platinum electrode a definite potential just as does a solution of ferric and ferrous ions. This reaction does not take place instantaneously; if hydrogen is deposited on the electrode, it is not immediately removed by the reaction and the electrode potential is therefore displaced from its equilibrium value according to the curves on Figure 46. The graph for the iodide-iodine electrode which shows only concentration polarization is added for comparison.[3] Chinhydron, an equimolecular compound of chinon and hydrochinon, was the initial solution.

The ease with which a substance in solution is reduced depends on its concentration, and on the electrode material in two ways: (1) on the catalytic effect of the electrode material, and (2) on the overvoltage. If cathodes of different materials are polarized in a solution containing an oxidizing substance, it is found that re-

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[1] Karaoglanoff, Z. Elektroch. **12**, 5 (1906); Le Blanc, Abhandlungen der deutschen Bunsen Gesellschaft **3**, 21 (1910).

[2] Chilesotti, Z. Elektroch. **12**, 146, 174, 197 (1906); Ott, Z. Elektroch. **18**, 349 (1912); Diethelm and Foerster, Z. phys. Ch. **62**, 129 (1908); Foerster and Yamasaki, Z. Elektroch. **17**, 366 (1911).

[3] Haber and Russ, Z. phys. Ch. **47**, 257 (1904).

duction begins to take place at different cathode potentials; that is, there are relative overvoltages for reducing any given oxidizing agent just as there are for the deposition of hydrogen. This is
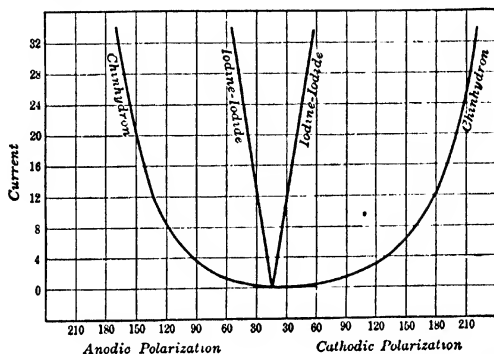
FIG. 46. — ANODIC AND CATHODIC OVERVOLTAGES FOR THE CHINHYDRON ELECTRODE AND FOR THE IODINE ELECTRODE

shown in Figure 47, which gives the current-density voltage curves of a normal solution of potassium nitrate for different cathodes.[1] It will be noticed that the voltages at which the current starts to increase rapidly on these metals is in the order of hydrogen over-
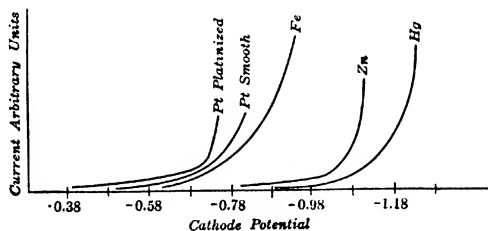
FIG. 47. — REDUCTION OF SOLUTION OF n-KNO$_3$ + 0.01-n-KOH

voltage, but this would not be so for the reductions of other substances. On platinized platinum electrodes the deposition of hydrogen takes place with greater ease than the reduction of

[1] Mueller, Z. anorg. Ch. **26**, 31 (1901); also Russ, Z. phys. Ch. **44**, 641 (1900).

nitrate, consequently very little reduction takes place on this electrode. When the reduction takes place more easily than deposition of hydrogen, the reduction increases in amount, as shown in Table 30.

TABLE 30. n-KNO$_3$.   ANODE AND CATHODE CURRENT DENSITY = 10 AMP./SQ.DM.   TEMP. 15–20° C.   ANODE, SMOOTH PLATINUM

CATHODE METAL	PERCENT HYDROGEN USED IN REDUCTION
Platinized platinum	15
Smooth platinum	76
Iron . . . . *	97.4
Zinc	96.5

Reduction of nitrate takes place to about the same extent on iron as in zinc, though the electrode potential is lower on iron than on zinc cathodes, which must be due to the greater catalyzing effect of the iron electrode.

Another example is that caffein is reduced more rapidly on mercury than on lead, while succinimid is reduced more rapidly on lead than on mercury, though the electrode potentials of both electrodes in pure acid are the same.[1]

Hydrogen overvoltage is of advantage in making the reduction of difficultly reducible substances possible by preventing the liberation of hydrogen in the gaseous state and thus reaching electrode potentials at which these difficult reductions take place.

The relation between the potential required for the deposition of hydrogen and that for a reduction is similar to the cases illustrated in Figures 36 and 37, where the reduction corresponds to the metal deposition.

Catalysis in the Electrode. — In some cases reduction is facilitated by the presence of a metal in solution that exists in two states of oxidation. The action consists in the electrolytic reduction of the metal to the lower state, which then acts on the other substance reducing it and being itself oxidized. The cycle is then repeated. An example of this is vanadic acid, which catalyzes the reduction of chloric acid, changing back and forth from vanadic acid to trivalent vanadium salt. Without this addition the reduction of chloric acid on platinum electrodes is very slow.[2]

[1] Tafel and Naumann, Z. phys. Ch. **50**, 713 (1905).
[2] Luther, Z. Elektroch. **13**, 437 (1907).

Titanium, copper, lead, mercury, and tin salts also act as catalyzers.[1]

In some cases the metal, in place of staying in solution during the cycle, is deposited at the cathode and reduces the substance in solution by its own oxidation from the metallic to the ionic state. Deposition and solution of the catalyzing metal takes place on the cathode simultaneously, but not at the same place. This might equally well be considered as a case of the catalytic effect of the metal of the cathode.

On the other hand certain additions to solutions prevent the reduction of reducible substances. One of the most efficient of these is alkali chromate, when its concentration is 0.1 to 0.2 percent of the electrolyte.[2] The presence of a chromate produces a thin film on the cathode of chromium oxide, which acts as a diaphragm. In strongly acid or strongly alkaline solutions, which dissolve this oxide, the protective action ceases.

Calcium and magnesium salts in neutral solutions produce a diaphragm of the hydrates of these metals which prevent reduction. This action can be improved by the addition of gelatin, starch, and white of egg; they are absorbed by the crystalline hydroxides and reduce the size of the crystals.[3] Magnesium cathodes prevent reduction, probably by the formation of a thin film of hydrate or oxide.[4]

The effect of increased temperature is to increase the velocity with which hydrogen deposited on the cathode reacts with the depolarizer, and therefore a high temperature increases the current density which can be used without evolving gaseous hydrogen. Since overvoltage decreases with increase in temperature it might be expected that for difficultly reducible substances requiring a high overvoltage an increase in temperature would cause the current efficiency to fall, but no such case seems to have been found.

The higher the current density the smaller is the concentration of the depolarizer on the surface of the cathode, and the more easily the depolarizer is reduced the higher the current density can be without evolving hydrogen. Therefore easily reducible substances give good current yields with high current density, but

[1] Elbs and Silbermann, Z. Elektroch. **7**, 589 (1901); Chilesotti, Z. Elektroch. **7**, 768 (1901).

[2] Imhoff, Germ. Pat. 110, 505 (1898); Mueller, Z. Elektroch. **5**, 469 (1899); **7**, 398 (1901); **8**, 909 (1902).

[3] Mueller and Buchner, Z. Elektroch. **16**, 93 (1910).

[4] Fr. Schmidt, Chem. Ztg. **33**, 991 (1909).

substances difficult to reduce give better results with low current density. An example is the reduction of nitrobenzol in 70 percent alcohol containing 2.5 g. of sodium acetate to give an alkaline reaction. At the boiling point the nitrobenzol is reduced to azobenzol, $C_6H_5N = NC_6H_5$, with 95 percent current efficiency with a current density of 10 amp./sq. dm. When all nitrobenzol is used up hydrogen evolution begins, but if the current density is reduced to 2 to 3 amp./sq. dm. the reduction continues to hydrazobenzol, $C_6H_5NH—NHC_6H_5$, with 90 percent current efficiency.[1]

ELECTROLYTIC OXIDATION

There are four kinds of oxidation corresponding to the four kinds of reduction:

(1) increase in the number of positive charges:

$$Fe^{++} + F = Fe^{+++} \quad or \quad 2\,Fe^{++} + O + H_2O = 2\,Fe^{+++} + 2\,OH^-;$$

(2) decrease in the number of negative charges:

$$MnO_4^{--} + F = MnO_4^-$$
$$or \qquad 2\,MnO_4^{--} + O + H_2O = 2\,MnO_4^- + 2\,OH^-;$$

(3) addition of oxygen:

$$SO_3^{--} + O = SO_4^{--};$$
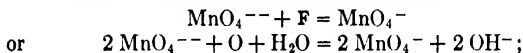
(4) removal of hydrogen:

$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O;$$
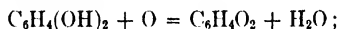
and (5) there is in addition a kind of oxidation to which there is no corresponding reduction, consisting in the doubling up of anions; which can be represented by any of the equations:

$$2\,HSO_4^- + O + H_2O = H_2S_2O_8 + 2\,OH^-,$$
$$or \qquad 2\,SO_4^{--} + 2\,F = S_2O_8^{--}$$
$$or \qquad 2\,HSO_4^- + 2\,F = H_2S_2O_8.$$
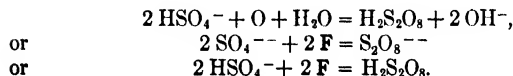
In (1) and (2) polarization occurs in amounts that vary greatly with the ions involved. Le Blanc found the results in Table 31 by means of the oscillograph.[2] They apply also to reduction.

[1] Elbs and Kopp, Z. Elektroch. **5**, 108 (1898).
[2] Abhandlungen der deutschen Bunsen Gesellschaft, **3**, 31 (1910).

TABLE 31. POLARIZATION OF ELECTRODE REACTIONS
INVOLVING ONLY CHANGE IN CHARGE

| | POLARIZATION IN MILLIVOLTS | |
| ELECTRODE | | |
	Platinum Electrode	Gold Electrode
Normal iodine-iodide	Scarcely detectable	Scarcely detectable
0.01-n-iodine-iodide	12–13	12–13
0.3 molal K_4FeCy_6 – K_3FeCy_6	Scarcely detectable	Scarcely detectable
0.01 molal K_4FeCy_6 – K_3FeCy_6	20	18.5
0.05 molal $KMnO_4$ – K_2MnO_4	3.5	5.0
0.5 molal $Fe_2(SO_4)_3$ – $FeSO_4$	Scarcely detectable	——
0.01 molal $Fe_2(SO_4)_3$ – $FeSO_4$	113	20
0.1 molal thallo-thallinitrate	290–730	520–800
0.16 molal cero-cerisulfate	370–580	420

Reversible organic reactions corresponding to (3) and (4) generally show more chemical polarization than (1) and (2) as shown by the graph for chinon-hydrochinon mixtures in Figure 46. Un-ionized organic bodies also react slowly with oxygen when the anode first becomes charged with oxygen, and consequently oxygen soon is evolved on the anode. This causes a further rise in the electrode potential difference, with the result that the oxidation becomes too powerful and is apt to oxidize the substance to carbon dioxide and water, the limit of oxidation.[1] For this reason electrolytic oxidation has not been much used for the oxidation of un-ionized organic substances. Examples where electrolytic oxidation can be used are the oxidation of hydrochinon to chinhydron, $C_6H_4O_2C_6H_4(OH)_2$, an intermediate product between hydrochinon and chinon, which takes place quantitatively, on platinum electrodes,[2] and the oxidation of aliphatic alcohols, aldehydes, and ketones.

That electrolytic oxidation is more powerful than any chemical oxidizing agent is shown by the fact that such bodies as persulfuric acid can be made in this way alone. The intensity of electrolytic oxidation can be modified by superimposing an alternating current on the direct.

As in the case of electrolytic reduction, in oxidation the yield is dependent on the concentration of the substance to be oxidized and on (1) the catalytic effect of the anode material and (2) on the

[1] See Foerster, *Elektrochemie wässeriger Lösungen*, p. 807 (1922).

[2] Liebmann, Z. Elektroch. **2**, 497 (1892).

oxygen overvoltage. A sufficiently high overvoltage is necessary, for in order to get a good efficiency it should of course be more difficult to liberate oxygen than to oxidize the depolarizer. An example of the catalytic effect of electrodes is the oxidation of chromium salts to chromic acid in sulfuric acid solution. The electrode potential difference of platinum anodes in an acid solution of a chromium salt is a little greater than that of a lead dioxide anode at the same current density, and still there is scarcely any oxidation to chromate on smooth platinum while on lead it takes place readily. On platinized platinum the potential difference is less than on smooth during this electrolysis, and yet the current yield is about one third of that on lead dioxide electrodes under similar conditions.[1]

Catalysts also affect electrolytic oxidations. While hydrochinon is oxidized to chinhydron in aqueous sulfuric acid solution as stated above, if a manganese salt is added the final product is chinon.[2]

Increase in temperature increases the velocity of depolarization for oxidation as it does for reduction, and it also reduces the overvoltage so that such high electrode potentials are not reached as at lower temperature. For substances reducible only at high electrode potentials this second effect may outweigh the first. Thus in a 2-n-KOH, 1-n-NaCOOH solution an increase in temperature from 16° to 75° lowers the yield from 95 percent to 10 percent on smooth platinum with a corresponding lowering in the cell voltage from 2.75 to 1.7 volts, but on iron anodes the same temperature rise increases the yield from 15 to 31 percent, while the cell voltage drops only from 1.99 to 1.83.[3]

The concentration of hydroxyl ions has an effect on electrolytic oxidation in two ways: (1) it is one of the factors in determining the electrode potential of an oxygen electrode, and (2) it may change the nature of the substance to be oxidized. The electrode potential of an oxygen electrode is higher in an acid than in an alkali solution because of the small number of hydroxyl ions in acid, and other things being equal a stronger oxidation would take place in acid than in alkali. If organic acids, which are slightly dissociated, are oxidized in acid solutions, it is principally the molecule that is exposed to the action. If, however, an organic acid is dissolved in an alkali, it changes to the highly dissociated

[1] Mueller and Soller, Z. Elektroch. **11**, 863 (1905).
[2] Germ. Pat. 117, 129 (1900).
[3] Foerster, Z. phys. Ch. **69**, 265 (1909).

salt and the anion of the salt is oxidized.   As an example may be mentioned that alkaline acetate solution is easily oxidized while acetic acid in a sulfuric acid solution is not oxidized at all in spite of the higher electrode potential in this case.[1]

Increase in current density has two opposing effects on electrolytic oxidation.   (1) It increases the electrode potential and consequently the intensity of the oxidizing power, but (2) in case no oxygen is liberated at low current density, an increase in current density may so diminish the concentration of the depolarizer that oxygen evolution starts and the current efficiency falls.   If oxygen is evolved from the start, the first may overbalance the second effect and increased current density may increase current efficiency.

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[1] Murray, J. Ch. Soc. **61**, 10 (1892).

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PART II

APPLIED ELECTROCHEMISTRY OF AQUEOUS SOLUTIONS

CHAPTER VII

ELECTROCHEMICAL ANALYSIS

THERE are four different electrical methods of quantitative analysis. These are (1) potential measurements, which give a means of determining the concentrations of ions too dilute to determine gravimetrically; (2) conductivity measurements, which is a method very convenient for determining concentrations of solutions; (3) titration with a galvanometer in place of an ordinary indicator, and finally (4) the ordinary electroanalysis, in which the metal is deposited on a platinum electrode and weighed.

Potential Measurements. — The principle of the first method has been explained in Part I. It consists in calculating concentrations by the Nernst equation from electromotive force measurements. For example, in place of calculating the electromotive force of the cell,

$$Ag|sol.\ AgNO_3|sol.\ KNO_3|sol.\ KCl,\ AgCl\ solid|Ag,$$
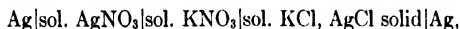
from concentrations of silver ions in the two solutions, as on page 71, the electromotive force can be measured and the unknown concentration calculated. This would then give a method of finding the solubility product of silver chloride and from this the solubility of silver chloride in water.

Conductivity Measurements. — The principle involved in analyzing a solution by conductivity measurement [1] is the same as when any other physical property, such as specific gravity, is used for the purpose; that is, the relation between the conductivity and quantity of substance in solution must be known. These data have already been obtained in a large number of cases and have been collected by Kohlrausch and Holborn. If the solution contains a single electrolyte whose conductivity at given concentrations has already been determined, all that is necessary is to interpolate graphically or arithmetically in the table. If, however, there is a maximum conductivity, as is generally the case,

[1] See Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte*, p. 131; Keller, Tr. Am. Electroch. Soc. **38**, 113 (1920).

there would be two possible concentrations for a given value of the conductivity. It is easy to tell on which side of the maximum such a solution lies by diluting a little and redetermining the conductivity. If the solution were more dilute than corresponds to the maximum value, further dilution would decrease the conductivity; if less dilute, the conductivity would be increased. In case the solution has a concentration near that of maximum conductivity, where the determination would be inaccurate, it can be diluted enough to remove it from this point, and the contents of the new solution determined. From this the concentration in the original one can be calculated.

This method has been shown to be useful in the determination of impurities in sugar and of mineral waters.[1] On account of the fact that the equivalent weights of the impurities likely to be present in mineral waters vary only within certain limits, it has been found that the quantity of the impurities can be estimated with a fair degree of accuracy from conductivity without analyzing the water to see which of the usual impurities are present.

This method is also useful in the case of mixtures of two salts when the conductivity of the mixture is the arithmetical mean of the single conductivities. This is often the case with nearly related compounds, which are generally difficult to separate chemically. For two substances for which this rule holds, having at equal concentrations the specific conductivities κ_1 and κ_2, the conductivity of a mixture of the same total concentration would have

the conductivity $\kappa = \dfrac{\kappa_1 p_1 + \kappa_2 p_2}{p_1 + p_2}$. By this means it has been

found possible to analyze satisfactorily mixtures of potassium chloride and bromide, and sulfates of potassium and rubidium.[2] Conductivity has also been applied extensively for the determination of the solubility of very insoluble salts.

Titration with a Galvanometer. — The use of a galvanometer as an indicator depends for the end point either on a sharp change in the resistance of the cell containing the solution titrated or in the change in the electrode potential of an electrode dipping in the solution. An example of the first case is the titration of silver nitrate with a standard solution of potassium chloride.[3] A measured quantity of a standard solution of potassium chloride is

[1] Reichert, Z. f. anal. Ch. **28**,1 (1889).
[2] Erdmann, B. B. **30**, 1175 (1897).
[3] Salomon, Z. f. Elektroch. **4**, 71 (1898).

placed in a beaker with two silver electrodes. In series with the two electrodes are connected a galvanometer and a source of electromotive force, which must be less than the decomposition value of the potassium chloride. On closing the circuit, only a very small residual current will be detected. On adding a little of the silver nitrate to the solution, silver chloride is precipitated, and a certain amount of silver ions, corresponding to the solubility of the chloride, will be in solution. We now have the cell

$$Ag|AgCl\ solution|Ag,$$
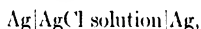
which has no decomposition point, but the quantity of silver is so small that the large resistance prevents the current from increasing to any great extent. As nitrate is added, the quantity of silver in solution changes very little until the last of the potassium chloride is used up. The first drop of silver nitrate in excess now increases the silver ions enormously, and there is a corresponding large increase in current, due to the reduced resistance of the cell. The following table shows the sharpness of the change.

Cubic Centimeters of $AgNO_3$	Galvanometer Reading
3.00	15
4.40	20
5.00	16
5.50	21
5.60	20
5.65	42

The use of a galvanometer as indicator when the electromotive force changes suddenly at the end point is illustrated by the following examples:[1] Suppose two beakers, one containing a tenth-normal solution of mercurous nitrate, the other a definite quantity of mercurous nitrate solution to be titrated, are connected by a siphon containing tenth-normal potassium nitrate. The bottom of each beaker is covered with a layer of mercury which makes contact with a platinum wire sealed in the glass. Such a cell would have the electromotive force $\dfrac{RT}{F} \log \dfrac{C_1}{C_2}$, where C_1 is the concentration of the mercury ions in the tenth-normal solution and C_2

[1] Behrend, Z. f. phys. Ch. **11**, 482 (1893).
For the titration of the halides in the presence of one another, see also Willard and Fenwick, J. Am. Ch. Soc. **45**, 623 (1923).

is their concentration in the unknown solution. If C_1 is equal to C_2, the electromotive force would be zero, but in general C_1 and C_2 would be somewhat different, so that there would be a reading in a galvanometer connected across the terminals of the cell. If a standard solution of potassium chloride is now added from a burette to the unknown solution, the concentration C_2 will be diminished, due to the precipitation of the mercury, and consequently the electromotive force will increase. As the end point is approached the change in electromotive force for each drop of potassium chloride added will be greater and greater, because of the larger percentage change in the concentration. With the drop of chloride which throws out the last of the mercury, the percentage change will be the greatest of all, and there will be a corresponding change in the reading of the galvanometer. The quantity of mercury ions now in the solution is due to the solubility of the mercury chloride. Since this solubility is diminished by adding a salt with a common ion, the electromotive force will continue to increase slowly on adding more chloride, but no further sudden change will occur. This change then indicates the end point. It is evident that this method would serve equally well to determine the strength of the chloride and that the titration can be carried out, starting with potassium chloride in one beaker in place of mercury nitrate. In this case there would be a decrease in voltage at the end point instead of an increase. Bromides can be titrated as well as chlorides, but a sharp end point is not obtained with iodides.

Since the determination of the end point depends on the concentration of the ions, the final volume of the solution must be kept within such limits that a drop of the solution from the burette will cause a marked change in the galvanometer reading. Starting with tenth-normal solutions, for this reason the final volume should not exceed 30 cubic centimeters, and therefore not over 10 cubic centimeters of the unknown solution should be taken for analysis. Since the end point can be obtained only to 0.05 cubic centimeter, this means an accuracy of 0.5 percent. In titrating potassium chloride the change in voltage at the end point is from 0.1 to 0.15 volt; in the case of the bromide it is 0.2 volt. Silver electrodes and silver nitrate can be used in place of mercury and mercury nitrates, and by this arrangement it is possible to determine directly the iodine in the presence of chloride and bromide, if an ammoniacal solution is used. Silver iodide, unlike silver chloride and bromide, is nearly insoluble in ammonia. Therefore on adding silver nitrate

to an ammoniacal solution of potassium chloride, bromide, and iodide, only the silver iodide will precipitate. When all the silver iodide is precipitated, there is a sudden change in the galvanometer reading. On acidifying, the combined amount of chloride and bromide may be determined. If also the total quantity of silver chloride, bromide, and iodide is weighed, the original amount of potassium chloride, bromide, and iodide can be calculated. This procedure, however, is not very accurate for the chloride and bromide, as is shown by the following analyses.[1]

	Grams Taken	Amount Found		Grams Taken	Amount Found
KCl	0.0223	0.0246	KCl	0.0448	0.0431
KBr	0.0359	0.0314	KBr	0.0354	0.3800
KI	0.0662	0.0666	KI	0.0167	0.0169
	0.1244	0.1226		0.0969	0.0980

An exactly similar method has been shown to be useful in the titration of acids and bases,[2] and for the determination of hydrogen ion concentrations in soils and waters. Neglecting the small potentials due to the liquid-liquid junctions, the electromotive force of the cell

$$\text{Pt} + \text{H}_2 \left| \begin{array}{c} \text{H}^+ \\ \text{conc. } C_1 \end{array} \right| \text{neutral salt} \left| \begin{array}{c} \text{H}^+ \\ \text{conc. } C_2 \end{array} \right| \text{H}_2 + \text{Pt} \\ \text{1 atm.}$$
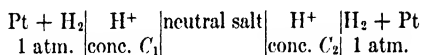
is given by the equation

$$\text{E} = \frac{RT}{F} \log \frac{C_1}{C_2}.$$

If alkali is now added to one of these acids, the hydrogen ion concentration diminishes, causing a gradual increase in the electromotive force. As in the cases described above, there will be a sudden change in the galvanometer reading when the end point is reached. The hydrogen electrode is shown in Figure 48,[3] and consists of palladium-plated gold, which gives more constant values than platinized platinum. The concentration of the hydrogen soon becomes constant in the electrode, as it is not absorbed by the

[1] Behrend, Z. f. phys. Ch. 11, 482 (1893).

For the titration of the halides in the presence of one another, see also Willard and Fenwick, J. Am. Ch. Soc. 45, 623 (1923).

[2] W. Böttger, Z. f. phys. Ch. 24, 253 (1897).

[3] Hildebrand, J. Am. Ch. Soc. 35, 847 (1913).

gold at all.   In place of a hydrogen electrode as standard in the above cell, a normal electrode would do equally well.

In carrying out a titration, the acid or alkali to be titrated is placed in a beaker and the hydrogen electrode put in position so that the palladium-plated gold is partly immersed. This electrode is then connected with the standard electrode and with some means for measuring the electromotive force; for example, a Lippmann electrometer and slide-wire bridge. Hydrogen is then bubbled over the hydrogen electrode till a constant potential is reached, which should require only a few minutes, and then alkali or acid, as the case may be, is added from the burette. After each addition the liquid is stirred up and

Fig. 48. — HILDEBRAND HYDROGEN ELECTRODE

the potential measured.   This will be found to increase gradually till the end point is reached, where there will be a sudden change in the potential.

Figure 49 [1] shows the change in electrode potential at the end point on titrating hydrochloric acid and acetic acid with sodium hydrate, and the hydrogen-ion concentrations corresponding to the voltages of the cell, which consists of a hydrogen electrode and a normal calomel electrode both dipping in the solution titrated.

The determination of hydrogen-ion concentrations by means of the hydrogen electrode has become quite common in biology and

[1] Hildebrand, J. Am. Ch. Soc. **35**, 847 (1913).

in water and soil analysis.[1] Complete apparatus designed for this purpose can be obtained ready for use.

In expressing the concentration of hydrogen ions in such analyses it is customary not to give the concentration but rather log $1/C_H$ and this is designated pH. Thus the concentration pH of hydrogen ions in pure water is log $1/10^{-7} = \log 10^7 = 7$.

It has been shown in Part I that the oxygen electrode does not give the true electrode potential of oxygen. The oxygen electrode, and the air electrode, have however been found useful in some cases,[2] such as for analyzing mixtures of chromate and dichromate. These do not of course give the hydrogen-ion concentration with the accuracy of the hydrogen electrode. About 0.5 on the scale explained above is the best that can be done.

FIG. 49. — TITRATION WITH A GALVANOMETER AS INDICATOR

Electroanalysis. — Electroanalysis is the fourth electrical method of analysis and consists in depositing the metal by electrolysis and weighing the deposit. This method of analysis was first pointed out by Cruikshank in 1801 but was very little used until the time of Walcott Gibbs[3] and of Luckow.[4]

The conditions under which metals are deposited from solutions of constant composition in forms suitable for weighing have already been explained, but in electroanalysis the concentration of the solution with respect to the metal deposited is not constant, and the solution may change in other respects, so that it does not necessarily follow that a metal can be determined by electroanaly-

[1] Gillespie, J. Wash. Acad. **6,** 7 (1916); W. W. Clark, *The Determination of Hydrogen Ions,* Baltimore (1920); Leed & Northrup Company's Catalog No. 75 (1920), Philadelphia.

[2] Furman, Tr. Am. Electroch. Soc. **43,** 79 (1923).

[3] Z. analyt. Ch. **3,** 334 (1864).

[4] Ding. polyt. J. **177,** 296 (1865).

sis because a good deposit is obtained from a solution of a certain concentration. Therefore electroanalysis requires a brief special discussion.

As stated above, the condition for the deposition of a metal is the following:

$$\frac{RT}{\nu F} \log \frac{P_M}{p_M} + \eta_M \leqq \frac{RT}{F} \log \frac{P_H}{p_{H^+}} + \eta_H, \qquad (1)$$

(1) Suppose we have an acid sulfate solute of a metal for which P_M is much smaller than P_H, to be electrolyzed between platinum electrodes. It is clear that as the metal deposits p_M diminishes and the electrode potential of the metal becomes more negative. Furthermore as the salt is decomposed sulfuric acid is set free and the electrode potential of hydrogen becomes less negative. It is therefore evidently impossible to deposit a metal completely, because the electrode potential of the metal must eventually equal that of hydrogen when the concentration of the metal becomes very small and the current then divides between hydrogen and metal. There are many metals for which P_M is so small that this does not happen until all metal except 0.1 mg. or less is deposited, which is less than the error of weighing, and is therefore sufficiently complete. These metals which can be determined quantitatively by electrodeposition, even from acid solution, include copper, silver, mercury, and bismuth.

(2) It is also possible to deposit a metal quantitatively, even if its molal electrode potential is more negative than that of hydrogen, by making the electrode potential required for the deposition of hydrogen more negative than that of the metal. This can be done by decreasing the value of p_H or by increasing η_H or both. Another method is to reduce P_M by depolarization by using a mercury cathode, which at the same time gives η_H a high value.[1]

In depositing a metal of this kind the relative amounts of current used to deposit hydrogen and metal vary with the values of η_M, η_H, p_M, and p_H, and all of these quantities vary with time as the electrolysis proceeds. When p_M becomes small nearly all of the current is used to deposit hydrogen, but this increases η_H with the result that more of the metal deposits. η_H can be still further increased by increasing the current as is frequently done toward the end of a deposition. The fact that at this stage most of the current is used to deposit hydrogen is the reason it takes longer to deposit a metal whose electrode is about equal that of hydrogen.

[1] E. F. Smith, *Electroanalysis*, p. 63 (1918).

The possibility of determining cadmium from a solution 2-normal in sulfuric acid is due to its high overvoltage for hydrogen, which in a solution normal in cadmium sulfate and 2-normal in sulfuric acid makes the voltage required to deposit hydrogen 0.4 to 0.6 volt more negative than that required for cadmium.[1] The corresponding value for zinc is only 0.2 volt, which is not sufficient for a quantitative separation, though zinc will deposit to a certain extent in a dilute, slightly acid solution.

For nickel the relation between the electrode potentials of metal and hydrogen are such that nickel can be deposited quantitatively from a neutral or slightly acid solution at a low current efficiency. The value of η_M is high and of η_H is low, so that though nickel is less negative than cadmium it takes longer to deposit quantitatively.[2] By heating to 75° C. η_M is reduced and the determination much facilitated.[3] It is of advantage also to neutralize the acid from time to time as formed by the decomposition of the salt.

If hydrogen-ion concentration must be reduced still more, alkaline solutions must be used. The heavy metals are precipitated as hydroxides in alkaline solutions, but in some cases can be redissolved as complex salts by an excess of alkalinity. The formation of complex salts also reduces p_M and can therefore be of no advantage unless the reduction of p_H is greater than that of p_M, as it is in a number of cases. Thus by changing cadmium to the complex ammonia salt cadmium becomes 0.2 volt more negative, but hydrogen in this solution becomes 0.5 volt more negative, which is a gain of 0.3 volt in the right direction.[4]

Where a metal is not soluble in alkali, other complex salts can be used from which the addition of alkali does not precipitate the hydroxide, or which have an alkaline reaction of their own, as potassium cyanide does. Other complex salts used in electroanalysis are sulfo-salts, such as K_2SnS_3, and compounds with salts of the alkali metals of oxalic, tartaric, citric, and pyrophosphoric acids. The complexity of a salt increases as the metal is deposited, because this leaves the complex-forming salt in large excess, and in some cases this excess has to be destroyed by the current before the metal can be completely deposited. This of course makes

[1] Beyer, Dissertation, Dresden (1906); Foerster, *Electrochemie wässeriger Lösungen*, p. 457 (1922).

[2] Denso, Z. Elektroch. **9**, 468 (1903).

[3] Schade, Dissertation, Dresden (1912); Foerster, *Electrochemie wässeriger Lösungen*, p. 457 (1922).

[4] Treadwell, *Elektroanalytische Methoden*, p. 126 (1915).

the process slow, but it can be speeded up by increasing the temperature. In depositing copper from a cyanide solution this increased rapidity is due to a reduction in η_M by the higher temperature. Other effects can be added to this as in the deposition of nickel from oxalate solution. Here high temperature increases the speed of oxidation of oxalate to ammonium carbonate, with the change of nickel from the complex $Ni(C_2O_4)_2^{--}$ to $Ni(NH_3)_6^{++}$ from which it is more easily deposited.[1]

Another reason for using complex salts is that they give smooth coherent deposits. In general, however, complex salts should be avoided when possible as they frequently cause too high a weight by being included in the deposit.

Of the mineral acids, sulfates are the best solutions to use because hydrogen is depolarized in solutions of chlorides and nitrates and the effect is then the same as though the concentration of acid were much increased.

In the separation of one metal from another, whose molal electrode potentials are on the same side of hydrogen, these must be so far apart that the concentration of one can be reduced to the desired amount before its electrode potential becomes as negative as that of the other metal. A voltage is applied to the cell sufficient to deposit the less negative metal practically completely but insufficient to deposit the second.[2]

When the electrode potentials of metals are on opposite sides of hydrogen, a constant current can be used, for when the less negative metal is completely deposited the current deposits hydrogen in place of the other metal. The relative values of electrode potentials of metals and of hydrogen can often be altered so as to make the electrode potential of hydrogen fall between those of metals whose molal electrode potentials are on the same side of hydrogen. An example of this is the separation of zinc from cadmium in an ammoniacal solution containing ammonium nitrate. The nitrate depolarizes hydrogen and neutralizes its high overvoltage on cadmium so that the deposition voltage of hydrogen lies between that of cadmium and zinc in this solution and these two metals can be separated with a constant current.[3]

In carrying out electroanalyses a platinum dish is generally used as cathode and an anode of platinum wire, as shown in Figure 50.

[1] Frueh, Dissertation, Dresden (1911); Foerster, *Electrochemie wässeriger Lösungen*, p. 459 (1922).

[2] Freudenberg, Z. phys. Ch. **12**, 97 (1893).

[3] Treadwell, *Elektroanalytische Methoden*, p. 190 (1915).

Stirring can be accomplished by rotating the anode and is very important as a means of reducing the time required for analysis. Copper determinations are carried out in 20 minutes [1] with stirring which would require 3 hours without.
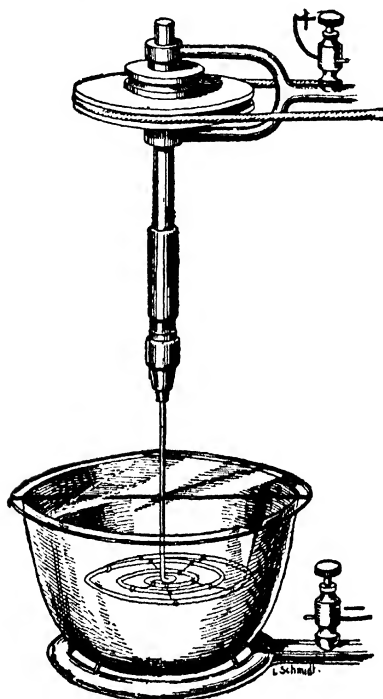
FIG. 50. — PLATINUM DISH FOR ELECTROANALYSIS

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[1] Fischer, *Elektrolytische Schnellmethoden* (1908).

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CHAPTER VIII

MATERIALS USED IN CONSTRUCTING
ELECTROLYTIC CELLS

Unattackable Electrodes. — In the extraction of metals and in all electrolytic work except metal refining, anodes are used which are not intended to dissolve. No anode, however, is entirely unattackable, and the material selected depends on the nature of the solution in which it is to be used.

Platinum is, perhaps, the most universally usable of any materials, especially when alloyed with 10 percent of iridium.[1] Electrolysis of this alloy as an anode in concentrated sodium chloride with a current density of 30 amp./sq. dm. and the passage of 1200 amp. hr. at 80° C. caused a loss of only 0.5 mg. per sq. dm. In hydrochloric acid a platinum anode is attacked more at a low than at a high current density, because at a high current density the acid in contact with the electrode becomes more dilute. With a current density of 2.76 amp./ sq. dm. in 32.5 percent hydrochloric acid at 25° C., 10.79 percent of the current dissolves platinum. If the current density is 200 amp./sq. dm., platinum is unattacked.[2]

For some work platinum black has been found superior to smooth platinum on account of the saving in voltage, but platinum black does not last well. On heating, it turns to gray platinum, and it has been found that if this is done at a low temperature, gray platinum lasts well and saves about 80 percent of the voltage saved by platinum black.[3]

Graphite and carbon are used as unattackable anodes in solutions which do not evolve much oxygen, for example, in the electrolysis of sodium chloride. Graphite is very slightly attacked by chlorine.

Table 32 shows the extent to which Acheson graphite and amorphous carbon are attacked in different solutions.

[1] Denso, Z. Elektroch. **8**, 149 (1902).
[2] Haber und Grindberg, Z. anorg. Ch. **16**, 446 (1898); Bran, Z. Elektroch. **8**, 197 (1902).
[3] Geibel, Z. Elektroch. **12**, 817 (1906).

TABLE 32.   CARBON AND ACHESON GRAPHITE ANODES [1]

ELECTROLYTE	PERCENT CURRENT EFFICIENCY OF OXIDATION OF ANODE	
	Graphite	Amorphous Carbon
2-n-NaOH (8 percent)	2	50–78
20 percent NaCl without diaphragm, containing chromate, 60° C.	7.4	12–41
20 percent H₂SO₄, 18° C.	94 96	85–97

In sodium hydrate the electrode potential at which oxygen is evolved is less than in acid and graphite is much less attacked than in acid. In acid, graphite is about as badly attacked as amorphous carbon.

By impregnating carbon with a solution of cobalt, the anodic voltage can be reduced several tenths of a volt in sodium hydrate solutions. The cobalt peroxide deposited in the pores catalyzes the oxygen evolution, and reduces the oxidizing intensity.[2]

It has been found that partially graphitized electrodes consisting of 75 percent graphite and 25 percent amorphous carbon show the least loss in weight, when used as anodes in sodium chloride solutions.[3] These electrodes are made by incomplete graphitization. They were tested by electrolyzing as anodes in a sodium chloride solution containing 250 g. NaCl and 20 g. chromate per liter with a current density of 6.7 amp./sq. dm. After the passage of 150 ampere hours the loss in weight was determined.

Both amorphous carbon and graphite are porous, so that electrolysis takes place not only on the surface but also within the pores. From 18 to 20 percent of the volume consists of pores. This can be determined by the amount of water absorbed. The sample should be heated to about 200° C. and plunged quickly in cold water so as to fill the pores with water. The surface is then dried and the volume of the sample determined by immersing in water in a burette. This gives the volume; from this and the weight dry the apparent specific gravity b is calculated. The true specific gravity a is found by boiling small pieces of known weight in a pyknometer to remove air, cooling, and filling the

[1] Foerster, Z. Elektroch. **8**, 146 (1902).

[2] Joost, Dissertation 1910, in Foerster, *Elektrochemie wässeriger Losungen*, p. 451 (1922).

[3] Arndt and Fehse, Z. Elektroch. **28**, 376 (1922).

pyknometer and weighing.[1] The percent porosity is then

$$100 \frac{(a - b)}{b}.$$

Anodes of fused magnetite have been used in the electrolysis of sodium chloride and in electrolyzing copper sulfate solutions. Hollow castings are made by pouring out the liquid inner part after a sufficient thickness of wall has solidified. The inside surface is copper plated to improve the conductance, which is rather low.[2]

These electrodes are very brittle, and are not entirely insoluble in 10 percent sulfuric acid. The addition of copper oxide makes stronger electrodes, and the improvement is proportional to the amount of copper oxide added up to 20 percent, the highest percent tested.[3]

Magnetite electrodes last for years as anodes in alkali chloride electrolysis without any apparent loss in weight.[4]

Lead anodes are scarcely to be distinguished from lead peroxide, because lead becomes covered with the peroxide on electrolyzing in an acid solution. Sometimes the peroxide layer is formed in a special solution. (See page 207.) They are used in sulfate solutions where chlorides, nitrates, and other substances that form soluble lead salts are absent.

Manganese dioxide can be made in the form of plates which are said to be remarkably resistant chemically. Manganese nitrate alone, or mixed with manganese dioxide, is molded in the proper form, peroxidized lead rods are inserted for connections, and the mixture is heated to 140° to 200° C. Manganese nitrate decomposes and forms a firm cake of fairly well-conducting dioxide.[5]

Both iron and nickel can be used as anodes in alkaline solutions. Duriron, a ferrosilicon alloy containing 13 percent silicon, was formerly used in sulfate solutions containing small amounts of chloride and nitrate, in which lead could not be used, in copper extraction at Chuquicamata, Chili. These anodes are brittle, and corrode at the rate of 5 to 6 percent of the weight of copper deposited.[6] In this solution ordinary lead would have a corrosion

[1] Zellner, *Die Künstlichen Kohlen*, p. 243 (1903).

[2] Speketer, B. B. **42**, 2899 (1909); E. Mueller, Z. angew. Ch. **23**, 216 (1910).

[3] Thompson and Atchison, Tr. Am. Electroch. Soc. **31**, 213 (1917).

[4] Askenasy, *Technische Elektrochemie*, **2**, 251 (1916).

[5] Siemens and Halske, Germ. Pat. 221,130 (1910); 235,234 (1911); Engelhardt, Metallurgie, **7**, 4 (1910).

[6] Fink and Eldridge, Tr. Am. Electroch. **40**, 51 (1921).

loss equal to 65 percent of the copper deposited, but if alloyed with 10 percent thallium and 20 percent tin, the corrosion loss is reduced to 1.2 percent of the copper deposited. The low loss is due to a film formed on the surface of the anode by electrolysis.

Silicon carbide electrodes are said to give good results in electrolyzing alkali chlorides, but they are not used to any extent.[1] Silicon is mixed with silicon carbide and glycerine as a binder and sintered to a uniform body, which is dense, resistant to temperature, and conducts well. Apparently a carbide is formed having less carbon than CSi.

Diaphragms. — In many electrolyses it is necessary to prevent mechanical mixing of the anolyte and catholyte, or to keep the electrolyte from the anode or from the cathode as much as possible. This is accomplished by placing a porous partition between the electrodes which allows the passage of the current. This partition, of course, does not prevent the migration of ions from one compartment to the other, and may cause the water to move through by electro-osmosis.
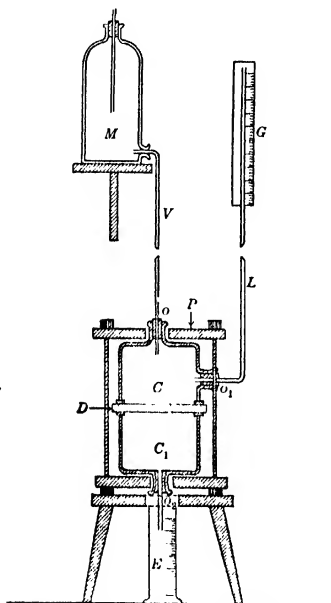
FIG. 51. — APPARATUS FOR TESTING DIAPHRAGMS

Diaphragms are made of the following substances: thin wood sheets to prevent short-circuiting the plates in storage batteries, asbestos paper and cloth, cement, burnt, unglazed clay, and other similar materials.

A good diaphragm should not have much resistance, should have fine pores, should withstand the action of the solution, and should

[1] Z. Elektroch. **13**, 2 (1907); Gebr. Siemens & Co., Germ. Pat. 177,252 (1906).

have mechanical strength. The volume of the pores of a diaphragm can be determined by weighing dry and after soaking in water. The volume of pores in various diaphragms varies from 22 to 70 percent. Pukall clay is about 30 percent pores.

The permeability, or the ease with which a liquid passes through it, can be determined by means of an apparatus as shown in Figure 51.[1] The diaphragm D is clamped between the two glass vessels CC and the upper one is filled with water, the head of which is measured on the scale G. Water percolates through the diaphragm and is collected in E. The coefficient of permeability K is the number of cubic centimeters of a liquid, whose coefficient of viscosity is η, which pass in one hour through a surface of one square decimeter under a pressure of one gram per square centimeter and is given by the equation,

$$K = \frac{V\eta}{Ah},$$

where V is the volume that passes per hour, A is the surface in square decimeters, and h is grams per square centimeter.

For determining diffusion a similar vessel is used, but the diaphragm is placed vertically, and there is no difference of level of the liquid on the two sides. The concentration of the solution on the two sides is different, and the amount which passes through in a given time while both solutions are stirred is measured.

The resistance of a diaphragm is determined by the difference in the resistance of a cell when the diaphragm is in place and when it is removed.

Good clay diaphragms were first produced by W. Pukall, but these are made mostly in the form of small cups for laboratory use. They are attacked considerably by hydrochloric acid and by alkalies above 50° C. Le Blanc succeeded in making a diaphragm that withstood the action of chromic acid in the regeneration of chrome alum,[2] and Buchner made diaphragms from kaolin and fused aluminum oxide that are not at all affected by acids.[3]

The General Filtration Company of Rochester, New York, make a diaphragm of " electro-filtros " in a standard size of 12 by 12 in., $\frac{1}{2}$ to 1 in. thick, which is not attacked by concentrated or dilute acids or by dilute alkalies.[4] It has a low resistance and

[1] Guye and Tardy, J. Chim. Phys. 2, 79 (1904).
[2] Z. Elektroch. 7, 653 (1900).
[3] Z. angew. Ch. 1904, p. 985.
[4] Thatcher, Chem. Met. Eng. 13, 336 (1915).

prevents mixing. It is made from pure fine silica cemented with a small amount of fused silicious binding material.

Electrolytic Cells. — The materials used in constructing electrolytic cells are principally wood lined with lead or asphalt ; slate, iron, and cement, or concrete with some non-porous lining. Wood with lead lining is used in the multiple system of metal refining in sulfuric acid solutions, but cannot be used for the electrolysis of chlorides. Slate can be used for the electrolysis of chlorides, but is expensive and requires great care in leveling and drawing together. Concrete is not expensive and is suitable for chloride electrolysis. The cement should be slow setting. It is tested by mixing a handful with water to a stiff paste and working it on a glass plate into a cake $\frac{1}{2}$ in. high and 3 to 4 in. in diameter. The surface is troweled smooth and the sides brought down to a thin edge. It is allowed to stand for a few hours and then covered with a wet cloth and left in a cool place over night. If it sets slowly and shows no cracks on the surface or edges, it is satisfactory. Crushed granite should be used for the best work. The size should be such that no piece has a larger diameter than one quarter of the thickness of the wall in which it is to be used. Pieces smaller than $\frac{1}{4}$ in. should be rejected as it interferes with filling the voids. The mixture consists of 4 parts rock, 2 parts sand, and 1 part cement, by volume. This should be rammed into the mold. Three or four days should elapse before removing the mold. If acid is to be used in the tank, it should be lined with paraffin or tar.[1]

Mastic concrete consists of ground quartz of all sizes held by " hermastic," a stiff asphaltic material. The stiffness depends on the percentage of quartz or other filler. With a high content of filler the mixture melts at 250° to 300° C., while the pure mastic melts at about 70° C. This concrete does not cost much more than ordinary Portland cement concrete but it must be mixed hot and poured in a melted state. It is acid proof and water proof.[2]

A lining made by the Vulcanite Paving Company of Philadelphia consists of a specially refined Trinidad asphalt mixture, with crushed quartz or granite. Continued contact with solution over 40° C. resulted in softening this mastic, particularly if any oil was present. It is not attacked by acids.[3]

Soapstone is used for making hypochlorite cells, by the Electro Chemical Company, of Dayton, Ohio.

[1] D. H. Browne, Electroch. Ind. 1, 273 (1903).
[2] Ralston, *Hydrometallurgy of Zinc*, p. 99 (1921).
[3] E. A. Cappelen Smith, Tr. Am. Electroch. Soc. **25**, 202 (1914).

CHAPTER IX

ELECTROPLATING, ELECTROTYPING, AND THE PRODUCTION OF METALLIC OBJECTS

ELECTROPLATING is the earliest of electrochemical industries. Brugnatelli observed gold plating as early as 1805, and by 1840 gold and silver plating began to be of technical importance,[1] but the invention of dynamos was necessary before this industry could grow to its present size. While gold and silver were the first metals used for plating, nickel plating began to be employed first in this country in the 70's;[2] more recently plating with copper, zinc, lead, and brass has been developed extensively.

Galvanoplasty, or the production of finished objects, was discovered by Jacobi of Petrograd in 1838. This industry has also grown to large proportions. It includes electrotyping, parabolic mirrors, seamless tubes of copper and of iron, the decoration of glass, china, and vulcanite with gold and silver, the production of phonograph records, small statues, and innumerable similar objects. It was estimated in 1914 that 15,000 tons of metals were used annually for electroplating and for galvanoplastic work.[3]

1. ELECTROPLATING

The equipment of an electroplating plant consists of a dynamo, tanks for plating, washing, and pickling, hoods to carry off fumes produced in pickling, buffing and grinding equipment, and dust collectors for carrying off the dirt produced in these operations, heated sawdust boxes for drying, ammeters, rheostats, a good water supply, steam heat for some of the solutions, and the necessary chemicals.

Dynamos for electroplating are made in different sizes to deliver from 50 amperes to several thousand, at 5 to 6 volts. Electro-

[1] See W. Siemens, *Lebenserrinnerungen,* p 25, for an interesting account of his discovery of gold plating from a thiosulfate solution.

[2] For an account of the origin of nickel plating in this country see Adams, Tr. Am. Electroch. Soc. **9**, 211 (1906). It was carried out by Boettger in Frankfurt in 1842.

[3] Pfanhauser, Z. Elektroch. **20**, 437 (1914).

plating tanks cannot be connected in series, for the removal of the cathodes from one tank in the series would break the current in the other tanks. Each tank is connected directly to the dynamo with an ammeter and rheostat in series.
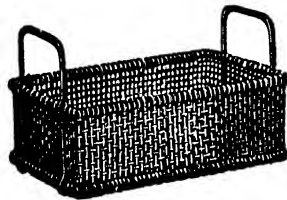
FIG. 52. — TRAY FOR PLATING SMALL OBJECTS

The floor of a plating room should be waterproof on account of the large amount of drippings from the objects when taken from the tanks. It is usual to have wooden plank walks raised an inch or two above the floor.

The tanks used for holding the plating solutions are usually of wood and are lined with lead or a mixture of pitch, resin, and linseed oil. The anodes are hung on brass bars running lengthwise with the tank, and the objects to be plated are hung on similar bars
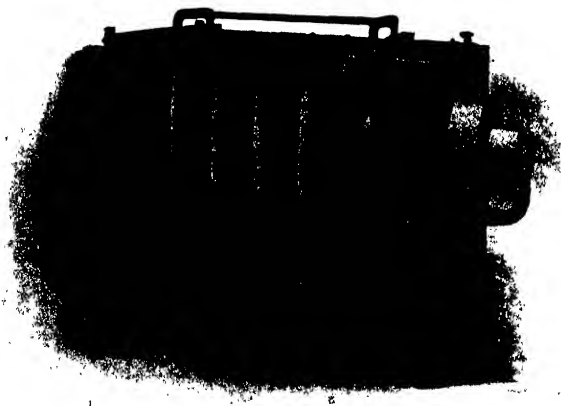
FIG. 53. — DRUM FOR PLATING SMALL OBJECTS

between two rows of anodes, in order to plate both sides uniformly. Small objects which are to be carefully plated are strung together in rows on wires and hung in the bath. Where not so much care is required, as in the case of small nails, it is sufficient to place them in a tray, shown in Figure 52, and hang them in the solution, or in a

drum whose sides are perforated, as in Figure 53. The drum turns on its axle slowly, and the current is conducted from the pile of small objects to the axle by metal strips. Of course the tray or the axle and metal strips are also plated.

Figure 54 shows the plating plant of the National Cash Register Company,[1] where plating with nickel, copper, silver, and zinc are all carried out.

In plating, the first step is to clean the surface thoroughly in order to make the deposit adhere well. Rough surfaces are occasionally plated for the purpose of protection, but more usually are first ground and polished.

The usual method of removing scale from sheet iron and other forms of iron that are to be covered with zinc consists in immersing in hot, strong sulfuric acid until the surface is clean. The acid attacks the iron below the scale, which consists of Fe_3O_4, and the hydrogen formed blows off the scale. This uses up acid and produces a large amount of ferrous sulfate for which there is no demand. By electrolyzing as cathode in hot sulfuric acid the scale is reduced to iron and very little iron or acid is used up.[2] This process was patented by C. J. Reed.

The hydrogen, however, makes the iron brittle. It is said that pickling as anode in 27 percent sulfuric acid at $60°$ C. cleans effectively without impairing the physical properties,[3] but it must also use up more iron and acid than cathode pickling. A sand blast and wire brushes are other means of cleaning surfaces mechanically. An efficient method of polishing is to use a tumbling barrel containing the objects to be polished with a soap solution and steel balls, but this is not suitable for large objects. Dry tumbling is also used with small pieces of leather with or without fine silica.

The next operation is the thorough removal of grease from the surface. This is done by dipping in a hot solution of sodium hydrate or carbonate, sometimes in benzine, or by electrolyzing as cathode in a solution of carbonate. The alkalinity produced by electrolysis removes grease, and the hydrogen reduces oxides and

[1] Met. Chem. Eng. **8**, 275 (1910). For design of a plating plant, see Pfanhauser, Metallurgie, **1**, 313 (1904).

[2] Hering, Met. Chem. Eng. **13**, 785 (1915); Thompson, Mahlman, Dodson, Tr. Am. Electroch. Soc. **31**, 181 (1917); Met. Chem. Eng. **17**, 713 (1918).

[3] Coulson, Tr. Am. Electroch. Soc. **32**, 237 (1917). Langdon and Grossmann, however, find that any kind of electrolytic pickling causes about the same degree of brittleness as simple immersion in the same acid for the same time. Tr. Am. Electroch. Soc. **37**, 574 (1920).
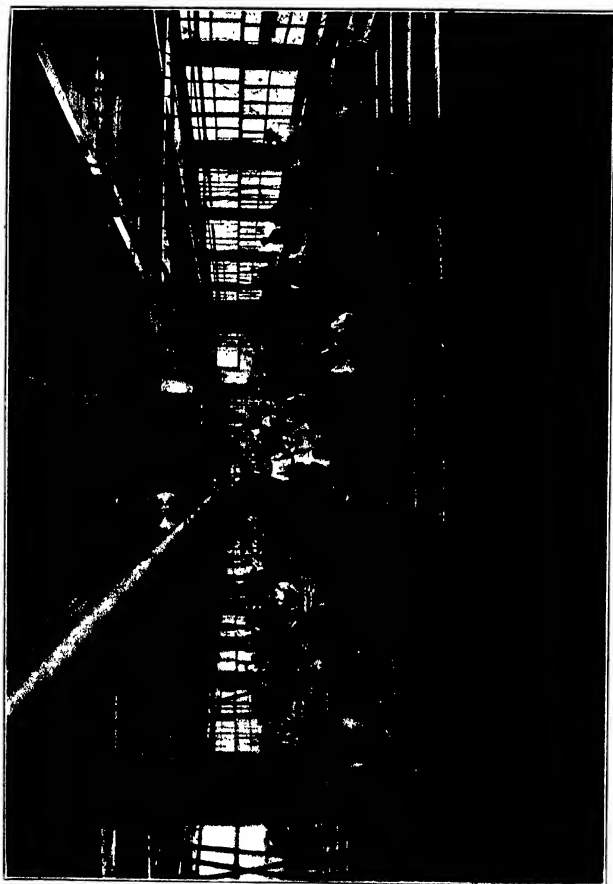
Fig. 54. — Plating Plant of the National Cash Register Company

carries away loose particles of oxide and grease.[1] This method
of cleaning requires a comparatively large current. After treat-
ment by one of these methods the surface to be plated is often
polished by brushes with Vienna lime and water.

Cleaning and plating may be done simultaneously, in a boil-
ing potassium cyanide solution containing copper or copper and
zinc.[2] This was begun about 1907 and is now widely practiced.
Its principal use is to give iron and steel a preliminary coating
before nickel plating. The hot alkaline cyanide dissolves grease
and where the surface is clean a good deposit of copper forms.
Any failure to remove grease is shown while still in the cleaning
bath by the absence of copper deposit on the uncleaned surface.
There is also a saving in time and labor in moving from one solu-
tion to another. The following cleaning and plating solution
can be used with or without zinc carbonate, depositing respectively
brass or copper.[3]

		Per Liter
The Hanson and Van Winkle Company's XXX lye	. . . . .	60 g.
Copper carbonate	. . . .	15 g.
Zinc carbonate	. . . .	15 g.
Ammonium carbonate	. . . .	30 g.
Potassium cyanide	. . . .	30 g.

The solution is used boiling.

After the removal of grease the alkali is washed off and the object
is dipped in a *pickle*, except when simultaneous plating and cleaning
are used. The purpose of a pickle is to make a bright surface, and
to remove any oxide formed by the alkali. The pickle varies with
the metal to be treated, since a solution which works well with one
metal is not necessarily suited to others. Cast iron and wrought
iron are pickled in a solution made by mixing 1 part by weight of
concentrated sulfuric acid with 15 parts of water.[4] A suitable
pickle for zinc is simply dilute sulfuric or hydrochloric acid.
Copper, brass, bronze, and German silver are treated with a
preliminary pickle consisting of 200 parts by weight of nitric acid
of specific gravity 1.33, 1 part of common salt, and 1 of lampblack.
The last ingredient has for its purpose the formation of nitrous

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[1] Burgess, El. World, **32**, 445 (1908).

[2] Watts, Tr. Am. Electroch. Soc. **27**, 141 (1915).

[3] Lovering, Metal Ind. 1913, p. 173.

[4] Langbein, *Electrodeposition of Metals*, 4th ed., p. 162. The English
measures used by Langbein are converted to the metric system when quoted.
Unless otherwise stated, the formulæ given for solutions in this chapter are
taken from the above work.

acid. After all impurities are removed by this bath, the object is washed in boiling water so that on removal it will dry quickly, and it is then immersed in a so-called *bright dipping bath*, to give a bright surface. This is made up of 75 parts by weight of nitric acid, of specific gravity 1.38, 100 parts of concentrated sulfuric acid, and 1 part of common salt. The object is then washed off in water and put while wet in the plating bath, where all electrical connections should have been made so that the plating begins immediately. Instead of the acid pickles following the removal of grease by alkali, brass is sometimes pickled in a hot solution of potassium cyanide, which dissolves the oxides, — somewhat more slowly than acid, — but it does not alter the polish. After the plating is finished the object is dipped in hot water and placed in warm sawdust to dry. In some cases the deposit is as bright as though it had been polished, but it is generally necessary to polish to give it this appearance.

Another important consideration is the possible action between the cathode metal and the plating solution. If a metal whose electrode potential is more negative than that dissolved in the plating solution is dipped in this solution, the dissolved metal will deposit on that immersed. Use is sometimes made of this in *plating by dipping*, which of course can give only thin layers, for when the underlying metal is covered, the action ceases. If the deposited metal does not adhere well to the underlying metal, the bath cannot be used for plating. This is the case with zinc dipping in solutions of simple salts of copper or silver. This difficulty can be overcome by using complex salts. Thus zinc placed in a solution of potassium cuprocyanide is covered with a smooth, well-adhering layer of copper, and can therefore be plated in this solution. This is probably due to the greater difficulty of depositing copper ions from a solution in which they are so dilute, and their consequent less rapid deposition by zinc; it is as though the current density were reduced. In case a metal like zinc is to be copper plated it would be given a preliminary coating of copper in a cyanide bath and the deposit would be thickened to the desired amount in a copper sulfate bath where the current efficiency is better.

A method of plating thin layers used for special purposes is plating by *contact*. This consists in connecting the metal to be plated with a more electronegative metal and dipping both in the plating solution. For example, if copper and zinc are connected and dipped in a silver cyanide bath, the copper is silver plated and zinc dissolves.

In order to remove the base metal as soon as possible from the action of the bath a " striking " bath is sometimes used, especially in silver plating. This is less concentrated than that used to thicken the deposit, and is run at a higher current density. As soon as the metal is completely covered it is removed and the plating is continued in the regular bath.

In order to get a deposit of uniform thickness it is necessary that the current density be uniform at all points at the cathode, but cathodes often have uneven surfaces, and even if flat, the current concentrates on edges. It has been shown above that with nearly all metals polarization increases with current density, consequently if the current density tends to be larger at one part of a cathode than at another, polarization tends to reduce it. This effect can be increased by using complex salts. In order to make it possible for current lines to penetrate to parts of the cathode surface farther from the anode, conducting salts are added to the solution, such as sulfates or chlorides of ammonium, sodium, or magnesium. A solution from which a metal deposits uniformly on uneven surfaces is said to " throw " well.[1]

The thickness of deposits varies according to the requirements from a few thousandths of a millimeter up to 0.2 mm.

The reason why an electrodeposited metal adheres to the underlying metal is in some cases doubtless due to alloying of the two.[2] The possibility of alloying does not, however, always insure good adherence, as shown by the fact that copper and nickel do not always stick well to iron. Too great a tendency to alloy is bad because the deposited metal is then slowly absorbed by the other and is as effectually removed as a covering as if it peeled off. Thus gold plated on lead or zinc soon disappears in the underlying metal. In cases of this kind the two easily alloying metals must be separated by a layer of another metal.

The concentrated solution from the anodes sinks to the bottom of the tank and the dilute solution rises to the top. To remedy this a solution in which much plating is done should be stirred at the end of each day's work; the anode mud will settle out again by morning.

It frequently happens that electrodeposits are pitted by bubbles of air becoming attached to the cathode and preventing the de-

[1] For a discussion of throwing power see Haring and Blum, Tr. Am. Electroch. Soc. **44**, 313 (1923).

[2] Electroch. Ind. **1**, 201 (1903); Haber, *Grundriss der technischen Elektrochemie*, p. 280 (1898).

position of metal beneath them. This can be obviated by boiling the solution to remove the dissolved air.[1]

It is difficult to get good results in plating on aluminum because of the ease with which aluminum coats itself with a film of oxide which prevents the metal from adhering well. One method of procedure is to immerse in a solution of potassium hydrate until hydrogen is evolved and then to amalgamate by dipping into a 0.5 percent solution of mercuric chloride immediately after treating with hydrate. The chloride is rinsed off and the object is then treated again with potassium hydrate and is then immediately suspended in a silvering bath,[2] or gilding bath, or a copper cyanide bath.

Nickel and Cobalt Plating. — Baths for nickel plating were formerly usually made from the rather difficultly soluble double salt $NiSO_4(NH_4)_2SO_4 \cdot 6 H_2O$. The small amount of nickel in this solution (a little over 1 percent) limited the current density for good deposits at room temperature to about 0.6 amp./sq. dm. This salt has consequently been more or less given up for more soluble salts. The following bath contains over 5 percent nickel and can be used at room temperature with any current density between 0.5 and 10 amp./sq. dm.[3]

$$NiSO_4 \cdot 6 H_2O \quad . \quad . \quad 240 \text{ g.}$$
$$NiCl_2 \cdot 6 H_2O \quad . \quad . \quad 15 \text{ g.}$$
$$H_3BO_3 \quad . \quad . \quad . \quad . \quad 30 \text{ g.}$$
$$H_2O \quad . \quad . \quad . \quad . \quad . \quad 1000 \text{ g.}$$

The small amount of nickel chloride is added to prevent the anodes from becoming passive. Nickel sulfate gives a more finely grained deposit than nickel chloride under the same conditions, and the deposit from the sulfate seems to protect the underlying metal better than the coarser deposit from nickel chloride. Langbein says baths containing chloride are not suitable for nickeling iron on account of its rusting.

The permissible amounts of zinc impurity allowable in nickel

[1] Watts, Tr. Am. Electroch. Soc. **35**, 279 (1919); Kern, *ibid.*, **13**, 107 (1908).

[2] Langbein, *Electrodeposition of Metals*, p. 591 (1920). For another procedure, see Burgess and Hambuechen, Electrochem. Ind. **2**, 85 (1904). Many others have been proposed.

[3] Hammond, Tr. Am. Electroch. Soc. **30**, 103 (1916). For an account of all important receipts to date, see Watts, Tr. Am. Electroch. **23**, 99 (1913). For the acidity of nickel-depositing solutions, see M. R. Thompson, Tr. Am. Electroch. Soc. **41**, 333 (1922).

sulfate for thin deposits is about 0.2 percent; for thick deposits, 0.1 percent. This does not allow for any accumulation. The maximum permissible amount of copper impurity for thin deposits made in less than one hour is 0.03 percent; for thick deposits up to 24 hours, 0.02 percent. This would correspond to 0.04 and 0.03 g./l. Most of the copper in nickel anodes goes irto the slime and so does not contaminate the bath.[1]

It has recently been found that the addition of fluoride makes a nickel-plating bath superior to any so far found.[2] The structure of the deposit is finer and at a current density not too high the deposit appears polished. It also has a higher tensile strength than when deposited from a chloride bath. This solution has the following composition:

GRAMS PER LITER

$$NiSO_4 \cdot 6 H_2O \quad . \quad . \ 281$$
$$NaF \quad . \quad . \quad . \quad . \quad . \ 8.4$$
$$H_3BO_3 \quad . \quad . \quad . \quad . \ 31$$

At 25° C. the specific resistance of the solution is 19.9 ohms per centimeter cube. The current density with this solution can be up to 4 amp./sq. dm. at room temperature in plating; for electrotyping the current density should not be over 2 amp./sq. dm. The effect of higher temperature is under investigation.

The current efficiency in both chloride and fluoride baths is over 99 percent with current densities up to 2 amp./sq. dm. At higher current densities the current efficiency is slightly better in fluoride than in chloride baths.

The composition of the deposit and that of "95 to 97 percent" nickel anodes used is the following:

	CAST ANODES PERCENT	CATHODE NICKEL	
		Chloride Bath, Percent	Fluoride Bath, Percent
Nickel + Cobalt . . .	97.5	99.60	99.40
Iron	0.60	0.27	0.45
Copper	0.20	0.09	0.15
Silicon	0.05	—	—
Carbon	1.50	—	—
	99.85	99.96	100.00

[1] M. R. Thompson and C. T. Thomas, Tr Am Electroch Soc. 42, 79 (1922).
[2] First commercially applied by E. G. Lovering. See Blum, Tr. Am. Electroch. Soc. 39, 459 (1921).

These anodes corrode well in fluoride solutions with the formation of scarcely any sludge. Hot rolled anodes also corrode well, but electrolytic anodes corrode poorly except in solutions so acid that the efficiency at the cathode becomes low. Anodes should be as pure as possible, for the deposition of iron with nickel is the principal cause of the deposit peeling. This is due to the fact that more iron is deposited in the first layer than in later ones and this unequal iron content produces strains which cause the nickel to curl and peel off.[1] This tendency may be counteracted by roughening the surface by etching or by some mechanical means, such as a sand blast, before depositing nickel.[2]

Iron is sometimes copper plated or brass plated before depositing nickel for the purpose of making the nickel adhere better, but nickel adheres well without this if the surface is well cleaned.

Black nickel plating can be applied directly to brass or copper.[3] Steel which is to be black nickel plated is first plated with copper or zinc. This plating is used for hardware, harness fittings, and other government equipment requiring a black or gray-black finish.

The following bath gives a uniform black deposit: 63 g. $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6 H_2O$, 7 g. NH_4CNS, 7 g. $ZnSO_4 \cdot 7 H_2O$, 1 l. water. Any acid should be neutralized with nickel carbonate.[4] This bath is operated at temperatures between 20° and 40° C., and at about one volt. At the end of about half an hour the surface is black and the plating is finished. A gray color indicates too high a current density.

Cobalt has nearly the same color as nickel with a slight reddish tinge. It is more expensive than nickel, and though it can be used in its place when nickel is scarce, as was recently the case in Germany, cobalt plating was given up as soon as the nickel shortage was past.[5]

Cobalt is deposited at a less negative voltage than nickel, but this is of no advantage for this voltage is lost in the rheostat if not in the bath. Cobalt anodes do not become passive as readily

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[1] Engemann, Z. Elektroch. **17**, 910 (1911). Some recent work by M. R. Thompson shows that if the acidity is properly controlled, the presence of iron in the solution does not necessarily cause cracking or peeling.   Tr. Am. Electroch. Soc. **44**, 359 (1923).

[2] Riedel, Z. Elektroch. **22**, 281 (1916).

[3] Blum, Tr. Am. Electroch. Soc. **34**, 169 (1918); Hogaboom, Slattery, and Ham, Bureau of Standards Technical Paper No. 190 (1921).

[4] Langbein, *l.c.* p. 319 (1920). Other formulæ are also given.

[5] Foerster, *Elektrochemie wässeriger Lösungen,* p. 494 (1922).

as nickel, but no difficulty is found with nickel in the presence of a little chloride. One of the disadvantages of cobalt is its greater tendency to peel.

A cobalt-plating bath can be made by substituting cobalt for nickel in the chloride bath given above. Whether fluoride would have a beneficial effect on cobalt, as it does on nickel, is not known. The cobalt baths proposed by Kalmus, Harper, and Savell [1] do not seem to have preserved their good qualities on continued use.

Copper and Brass Plating. — Copper plating is usually carried out as a preparation for the deposition of another metal. A cyanide bath is always used in order to prevent the formation of loose, powdery, or spongy deposits by more electronegative metals, such as iron or zinc, which would form if these metals were dipped in a sulfate bath. A sulfate bath could be used for iron, however, if the iron is first dipped in a hydrochloric acid solution of arsenious oxide containing from 10 to 60 grams of the oxide per liter. The acid may be concentrated or diluted with as much as two volumes of water.[2] Iron is thereby protected by a thin layer of arsenic which prevents the deposition of copper in an undesirable form when dipped in copper sulfate.

Copper cyanide baths are often made by dissolving cupric sulfate or acetate and adding potassium cyanide. Unless some oxidizable salt is present, this would result in the evolution of cyanogen when cupric changes to cuprous cyanide:

$$2\ CuSO_4 + 4\ KCN = 2\ CuCN + (CN)_2 + K_2SO_4.$$
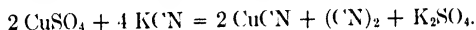
Acid sodium sulfite is the salt usually added to take up the cyanogen. The following bath is recommended by Pfanhauser:[3]

> 1 l. water
> 10 g. calcined sodium carbonate
> 20 g. sodium sulfate
> 20 g. acid sodium sulfite
> 30 g. potassium cuprocyanide
> 1 g. potassium cyanide

About 3 volts are applied, and the current density is about 0.3 amp./sq. dm. The current efficiency is 80 percent.

[1] Tr. Am. Electroch. Soc. **27**, 75 (1915).
[2] Discovered by J. Sitka. See Watts, Tr. Am. Electroch. Soc. **35**, 265 (1919).
[3] Schlötter, *Galvanostegie*, p. 136 (1910); Foerster, *Elektrochemie wässeriger Lösungen*, p. 495 (1922).

Sulfite is added to this bath to prevent the formation of insulating layers of cuprocupricyanide at the anode. Cyanide is gradually oxidized to carbonate at the anode and must be renewed from time to time.

Brass plating is used as a substitute for copper as an intermediate step and also as an ornamental covering. The following bath is recommended by Pfanhauser: [1]

> 1 l. water
> 14 g. calcined sodium carbonate
> 20 g. sodium sulfate
> 20 g. potassium cuprocyanide
> 20 g. potassium zinc cyanide
> 20 g. acid sodium sulfite
> 1 g. potassium cyanide
> 2 g. ammonium chloride

The current density is 0.3 amp./sq. dm. at about 3 volts, the temperature is between 15° and 20° C., and the cathode current efficiency is about 73 percent. Brass anodes are used.

The reasons why zinc and copper deposit together from a cyanide solution, and the effects of change in current density and in the ratio of copper to zinc in solution on the composition of the brass deposit have been given above (p. 122).

Zinc Plating. — A zinc covering is very useful as a protection for iron. It has the advantage over tin for this purpose that it is more electronegative than iron, so that in case a part of the iron becomes exposed and wet, zinc tends to dissolve in place of the iron. Iron is covered with zinc by the two methods of electroplating and of dipping in a bath of melted zinc. A third method, called sherardizing, consists in heating objects in zinc dust to 300° C.[2] The zinc deposited electrolytically is not so bright and pleasing in appearance as the dipped zinc, but it has been shown to protect the iron much more thoroughly.[3] A good solution for zinc plating is 200 grams of zinc sulfate, $ZnSO_4 \cdot 7 H_2O$, 40 grams of sodium sulfate, $Na_2SO_4 \cdot 10 H_2O$, 10 grams of zinc chloride, and 0.5 gram of boric acid per liter. The current density is from ½ to 2 amperes per square decimeter. The anodes are of zinc. Since a little more zinc dissolves than is deposited, the solution

[1] Schlötter, *Galvanostegie*, p. 238 (1910).

[2] Electrochem. and Met. Ind. **5**, 187 (1907).

[3] Burgess, Electrochem. and Met. Ind. **3**, 17 (1905); Szirmay, Z. Elektroch. **11**, 335 (1905).

would lose its acidity unless a small amount of acid is added as it is used up. The resistance may be reduced by warming to 40° or 45° C.[1]

According to some recent experiments[2] zinc deposited from a cyanide solution gives better protection than that from a sulfate bath. The solution recommended is as follows:

	GRAMS PER LITER
Zinc cyanide	60
Sodium cyanide	52.5
Sodium hydroxide	7.5 to 15
Sodium carbonate	30
Sodium fluoride	7.5
Corn sugar	7.5
Gum arabic	1.1

The temperature is from 40° to 50° C.; the voltage 3 to 5 volts depending on the current; and the current density is 4 amp./sq. dm. The cathode current efficiency is between 50 and 75 percent, while the anode efficiency is from 90 to 110 percent. Sodium cyanide must be added frequently in small quantities to make up for that used in local action with zinc. It is stated that zinc cyanide must also be added, but there seems no reason for this if more zinc dissolves than is deposited; on the contrary it would seem that zinc would have to be removed from time to time. Corn sugar and gum arabic are used up and are added when the necessity for them is shown by the color of the deposit.

The reasons given for the better protecting quality of zinc from a cyanide bath are (1) that the alkalinity keeps iron passive while in a sulfate bath the acidity tends to cause iron to rust, and (2) the deposit from cyanide is less porous than from sulfate.

The most reliable method of testing zinc protective coatings is known as the " salt-spray test," in which the plated surface is exposed to a spray of a 20 percent sodium chloride solution until rusting appears.[3] It was found that sheet iron plated in a cyanide bath until the deposit weighed 0.57 gram per square decimeter lasted 128 hours before showing rusting, while a similar piece with a coating from a sulfate bath weighing 0.75 gram per square decimeter lasted only 60 hours.

[1] Foerster, *Elektrochemie wässeriger Losungen*, p. 500 (1922).
[2] Werlund, Tr. Am. Electroch. Soc. **40**, 257 (1921) For other formulæ see Horsch and Fuwa, Tr. Am. Electroch. Soc. **41**, 363 (1922)
[3] Bureau of Standards Circular No. 80, Protective Metallic Coating for the Rustproofing of Iron and Steel (1922), or Langbein, *l.c.* 551 (1920).

Lead Plating. — Previous to the war there were only a few plants in the United States that plated lead commercially, and these were mostly for storage-battery fittings. During the war it developed greatly as a means of protecting the inside of gas shells.[1] The solutions are made either from lead fluosilicate or fluoborate. Lead can be deposited from a fluoborate bath directly on steel without an intermediate layer of copper, while a fluosilicate bath requires a preliminary copper coating. A fluoborate bath is made as follows:

	GRAMS PER LITER
Basic lead carbonate $PbCO_3 \cdot Pb(OH)_2$	142
50 percent hydrofluoric acid	240
Boric acid	116
Glue	0.2

The current density is about 3 amp./sq. dm. for light deposits and 2 amp./sq. dm. for heavy. The bath is used at room temperature. The best way to prepare the surface for lead plating is sandblasting.

It is believed that there is a large field for the future application of lead plating.

Silver Plating. — A satisfactory silver-plating bath is made by dissolving 25 grams of silver cyanide and 25 grams of potassium cyanide in one liter.[2] The current density is 0.1 to 0.45 amp./sq. dm. at one volt. Silver anodes are used.

Only copper or copper alloys are silver plated directly, and even these have to have a preliminary coating of mercury deposited by dipping in a " quicking " bath consisting of 25 grams of mercury potassium cyanide and 25 grams of potassium cyanide per liter. The surface is then rinsed off in water and is placed in a striking bath for 15 to 30 seconds. This bath consists of 60 grams of potassium cyanide and 3.4 grams of silver cyanide to one liter of water. The deposit is then thickened in the regular bath. The object of the striking bath is to make the deposit adhere better.

Silver deposited from a cyanide bath is usually of milk-white appearance and requires polishing, but the addition of carbon bisulfide causes silver to deposit bright, so that buffing is not necessary, if the current density is right. That this deposit is sensitive to change in current density is shown by the fact that

[1] Reeve, Tr. Am. Electroch. Soc. **35**, 389 (1919); Blum, Tr. Am. Electroch. Soc. **36**, 243 (1919).

[2] For all silver and gold-plating baths proposed see Frary, Tr. Am. Electroch. Soc. **23**, 62 (1913).

an object which is plating bright on a flat surface may not be bright on the edges where the current density is higher. The carbon bisulfide is first dissolved in a small amount of the silver solution and this is added to the bath. This preliminary carbon bisulfide solution is prepared by shaking ten drops of bisulfide in a liter of silver solution taken from the plating bath and allowing to settle over night; 0.3 gram of this is then added to each liter of the plating bath, and is replaced from time to time as the bisulfide is used up.

It is customary to hang objects on movable supports during silver plating, so they can be moved slowly back and forth in the bath.

Articles to be silver plated are now mostly made from German silver or some white metal so that if the silver wears off the underlying metal does not show so plainly as if it were copper or brass.

The electrode potential at which silver is deposited from a cyanide solution containing 0.1 mol $KAgCy_2$ and 0.2 mol KCN per liter is about -0.42 volt for current densities between 0.05 and 0.5 amp./sq. dm. at 18° C. and is about -0.70 if potassium cyanide is increased to 4 mols per liter, while the electrode potential at which hydrogen deposits from cyanide solutions is more negative than -1 volt. Consequently scarcely any hydrogen is evolved and the current efficiency for silver plating is nearly 100 percent.[1]

Gold Plating. — Gold plating is carried out both in hot and in cold solutions. Large articles are usually plated in cold baths, small articles in hot. Hot solutions give a denser deposit and a richer color. A less concentrated solution is used in hot gilding than in cold. Langbein gives the following bath for cold gilding: 3.7 g. gold as fulminating gold and 5 to 15 g. of potassium cyanide per liter. The current density is 0.15 amp./sq. dm. Fulminating gold is made by precipitating gold chloride with ammonia as long as a yellowish brown precipitate forms. This is washed and dissolved in potassium cyanide without allowing to dry. Most directions say to boil off the ammonia, but there seems to be no reason for so doing.[2]

A bath for hot gilding contains 1 gram of gold as fulminating gold per liter and 5 grams of potassium cyanide. The current density is 0.1 amp./sq. dm. and the temperature is between 70° and 80° C.

[1] Foerster, *Elektrochemie wässeriger Lösungen*, p. 498 (1922).
[2] Frary, Tr. Am. Electroch. Soc. **23**, 37 (1913).

Gold anodes are used and dissolve with 100 percent efficiency as long as the free potassium cyanide does not exceed 3 percent. At higher concentrations gold anodes become passive on account of a layer of insoluble $NaAuCy_2$ which comes from sodium always present in potassium cyanide. At much higher concentrations gold anodes become active again.[1]

Other Metals. — The Udylite [2] process for cadmium plating consists in depositing from a cyanide solution, washing, and baking at 150° to 200° C. The anodes are graphite, and cadmium hydroxide is added to keep up the strength. The current density with 10.5 percent cadmium is 2.7 to 31 amp./sq. dm. This coating is said to be superior to zinc for protecting iron and steel.[3]

Chromium can be plated from a 25 percent solution of chromic acid containing half a percent of chromic sulfate to any desired thickness. It is not as yet carried out commercially.[4] The yield is about 0.1 g./amp. hr. and it may fall considerably below this.

Iron plating for strengthening electrotypes has been used in Petrograd since before 1870.[5] The solution used was due to Klein, and contained ferrous sulfate and magnesium sulfate. With 0.5 gram-mol of each sulfate in a liter of solution, perfect deposits are obtained with a current density of 0.25 amp./sq. dm.[6]

GALVANOPLASTY

The following are some of the important galvanoplastic processes.

Electrotyping. — The first operation in making an exact duplicate of type set up ready for printing is to take an impression of the type in wax. The wax sometimes used is ozokerite. The thickness of the sheet of wax used for the purpose is about half an inch. After this has been carefully inspected to see that every letter is perfect, fine graphite powder is well worked into the surface by soft brushes. This is done in several operations, by machines and by hand. Iron filings are then sprinkled over this surface and a solution of copper sulfate is poured over it to produce a thin layer of copper, which will make the whole surface more conducting

[1] Coehn and Jacobsen, Z. anorg. Ch. **55**, 321 (1907).

[2] The Monthly Rev. **9**; No. 6, and No. 7, p. 14 (1922); Met. Ind. **20**, 356 and 469 (1922); U. S. Pat. 1383174, 5 and 6 (1921).

[3] Bureau of Standards Circular 80, p. 7 (1922).

[4] Sargent, Tr. Am. Electroch. Soc. **37**, 479 (1920).

[5] Jacobi, Brit. Ass. Rep. 1869, p. 67; Roberts-Austen, J. Iron and Steel Inst. 1887, II, p. 71.

[6] Haber, Z. Elektroch. **4**, 413 (1898).

than the graphite could do. This is an example of the use of plating by contact, explained above. The sheet is then hung in an acid copper sulfate bath, containing 200 to 250 g./l. of copper sulfate and 50 to 80 g./l. of free sulfuric acid, and is electrolyzed at room temperature at a current density of 5 to 9 amp./sq. dm. until the deposit is 0.15 to 0.25 mm. thick. At 35° C. the current density should be 8 to 10 amp./sq. dm.[1] It is then removed from the tank, and the wax is warmed and separated from the thin copper sheet. The copper is next backed to give it mechanical strength by pouring on it an alloy of lead and antimony. The subsequent purely mechanical operations of making the sheet perfectly level, so that each letter will print, and of mounting them on wood need not be described in this place. The advantages of electrotyping are the saving of wear on the type, and the fact that a small stock of type will prepare unlimited number of pages; for when a page is electrotyped, the type used for preparing this page may be used over again for another. Nearly all books are now printed in this way.

Wax negatives are not accurate enough for all electrotyping work, such as engraving plates for government bond issues. To attain the accuracy required in this work it is necessary to make a metal in place of a wax negative by plating nickel on the steel plate to be copied, after cleaning and brushing with graphite to permit subsequent separation.[2] Nickel is deposited on this surface and then alternate layers of nickel and copper, as it has been found this gives a much stronger plate than pure copper. The final plate used for printing is made by depositing an initial coat of nickel on this negative for 6 hours at 2 amp./sq. dm., giving a thickness of about 0.13 mm. Alternate depositions of nickel and copper for periods of one hour are then continued for six days. The current density for copper is 5.4 amp./sq. dm. so that the relative thickness is about 1 to 3; that is, the plate contains about 25 percent nickel. After a final deposition of copper for two days the plates are separated.

Copper Tubes,[3] Foil, and Wire. — Tubes are produced by depositing copper evenly on a cylindrical cathode, and the copper is re-

[1] Blum, Holler, and Rawden, Tr. Am. Electroch. Soc. **30**, 159 (1916). Directions for operating electrotyping baths are given in Bureau of Standards, Circular No. 52, 2nd ed.

[2] Blum and Slattery, Chem. Met. Eng. **25**, 320 (1911), and Blum, Structure of Alternately Deposited Metals, Tr. Am. Electroch. Soc. **40**, 307 (1921).

[3] See Pfanhauser, *Die Herstellung von Metallgegenständen auf Elektrolytischem Wege*, Engelhardt Monographs, Vol. 5 (1903).

moved when it has become sufficiently thick. In order to keep
the outer surface of the tube smooth, it must be polished during
the electrolysis; this is done in the Elmore [1] process by means of
an agate wheel whose edge
bears on the tube, as shown
in Figure 55. The wheel
turns on its axis and polishes
the surface over which it trav-
els. In the process of the
Société des Cuivres de France,
the polishing is obtained by
allowing two tubes to rotate
in contact with each other.
Polishing not only keeps the
surface smooth, but also
makes the use of higher cur-
rent densities possible.

Fig. 55. — Agate Wheel for Polishing
during Electrolysis

The tubes made by the
Elmore process are usually 3
meters long and vary up to 1.6 meters in diameter.[2] In order to
separate the finished tube from the axle, the surface of the axle
must be specially prepared so as to conduct and yet not make the
contact with the copper deposited too intimate. This may be done
by slightly oxidizing the metal on which the copper is precipitated.
The tube can then be worked loose by pressure.

In the Cowper-Coles process the mandrels are vertical and are
rotated in a vat shaped like an annular ring. In this way the
bearings are kept out of the solution. A current density of
20 amp./sq. dm. is used. For making sheet copper the cylinders
are 6 feet in diameter. Copper wire can be made by scratch-
ing the mandrel with a slight but angular spiral scratch with a
·pitch equal to the diameter of the wire to be made. The de-
posit forms a plane of cleavage at the apex of the scratch and
can be unwound and drawn through a die.[3] See also under iron
extraction.

In 1891, J. W. Swan patented a method of producing copper
wire, which consists in depositing copper on a wire so as to thicken
it, and in then drawing down the wire to the original size. The
apparatus is so planned that this is a continuous process.

[1] Electrochemist and Metallurgist, **3**, 151 (1903).
[2] Pfanhauser, *l.c.* p. 109.
[3] Electroch. Met. Ind. **6**, 412 (1908).

Parabolic Mirrors. — The production of parabolic mirrors has been worked out by Sherard Cowper-Coles.[1] It saves the expensive grinding of a parabolic surface for each mirror, for by this method any number of parabolic mirrors can be produced from one mold. The details of the process are the following: First a perfectly parabolic glass surface is prepared by pressing a glass plate about 3 centimeters thick, and hot enough to be soft, into a cast-iron mold of approximately a parabolic form. The glass surface which was next the iron is now made perfectly parabolic by polishing on a lathe with more refined means as the surface approaches nearer to perfection. The next step is to clean the surface and to silver it. The glass form, covered on the parabolic side with silver, is then placed in a copper sulfate bath, rotated slowly, and copper plated to give the mirror mechanical strength. In order to separate the metal from the glass, they are placed in a water bath and heated to 50° C. The unequal expansion easily separates the glass from the metal. The concave side is now a perfect mirror, but the silver would soon tarnish and must therefore be protected by a thin layer of platinum deposited on the silver electrolytically, from a solution of ammonium platinic chloride in sodium citrate. The mirror is then mounted.

In covering glass or china with gold or silver decorations that part of the surface to be covered is made conducting by painting on a metal film and burning it in. Glass, for example, is heated until it softens slightly. It is then a simple matter to thicken this deposit so that it can be engraved or finished in any way desired.

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[1] See Coles, Engelhardt Monographs, Vol. 14 (1904).

CHAPTER X

ELECTROLYTIC EXTRACTION AND REFINING OF METALS

THE EXTRACTION OF METALS

Electrolytic Copper Extraction. — The first attempts to extract metals from their ores electrolytically were failures either because the methods were fundamentally wrong or because of technical difficulties.

The Marchese process [1] is an example of a method fundamentally wrong. This was an attempt to electrolyze a poorly conducting copper matte as anode for the purpose of extracting copper. The matte from which the copper was to be extracted had the following composition:

Copper 17.20	percent
Lead 23.70	percent
Iron 29.18	percent
Sulfur 21.03	percent
SO_3 . . . . 0.69	percent
Silica 0.88	percent
Silver 0.062	percent

The solution was obtained by treating a matte similar to the above with dilute sulfuric acid, and consisted principally of copper and ferrous sulfates. On electrolyzing, copper deposits on the cathode and copper and iron are dissolved at the anode as sulfates. In order to make the oxidizing power of ferric sulfate available, the matte from which the solution is made is treated with the electrolyte in which ferric sulfate has accumulated. The ferric sulfate is reduced to ferrous sulfate, and cuprous sulfide and oxide is changed to copper sulfate. The solution is then returned to the electrolyzing baths.

Favorable results were obtained in the laboratory in Genoa, and on a larger scale at Stolberg from February to April, 1885. The copper obtained was 99.92 percent pure. A large plant was then built to produce 500 to 600 kilograms of copper in 24 hours with 58 vats, 2.2 meters long, 1 meter deep, and 1 meter

[1] Cohen, Z. f. Elektroch. **1**, 50 (1894).

wide. At first all expectations were realized. The baths worked well and the copper produced was pure. Within a few days, however, the voltage across the baths began to rise, in some cases to 5 volts. This was due to the deposition of sulfur on the anode and the disintegration of the anode due to the dissolving of the copper and iron. Large pieces became detached from the anode and fell to the bottom of the tank, filling up the space between anode and cathode and producing a short circuit. The copper also became impure, containing antimony, bismuth, lead, iron, zinc, and sulfur. Insoluble lead electrodes were then tried, but the polarization due to the formation of lead peroxide was excessive, and the yield in copper fell to 60 percent of the theoretical amount. If a matte consisting of nearly pure cuprous sulfide is used, the process can be operated as shown by Borchers, Franke, and Guenther, but the anodes do not dissolve evenly and the cost is prohibitive.[1]

The Siemens and Halske process was then tried by the same company. The principal difference between this and the Marchese process is the use of insoluble anodes and the separation of anode and cathode by a diaphragm. Copper is deposited from a solution containing ferrous sulfate and copper sulfate. The solution then circulates to the anode, where ferrous sulfate is oxidized to the ferric state. The oxidized solution is then used to dissolve more copper from the ore. For three months an attempt was made to carry out this process, but it was finally given up, partly at least on account of mechanical difficulties, such as the tearing of the diaphragm and disintegration of the carbon anodes   A 33-day test of the Siemens and Halske process was made in 1913 at the Ray mine in Arizona, but it was not continued.[2]

The Hoepfner[3] process is similar in principle to the Siemens and Halske process. The unroasted ore is dissolved by cupric chloride, and the cupric chloride is reduced to cuprous chloride. This is kept in solution by sodium chloride. The action of the cupric chloride is the following:[4]

$$Cu_2S + 2 CuCl_2 = 4 CuCl + S, \text{ or } CuS + CuCl_2 = 2 CuCl + S.$$
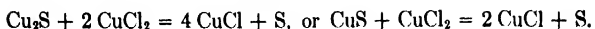
The solution containing cuprous chloride is electrolyzed in the cathode compartment, where it loses part of its copper. The solution then circulates to the anode compartment, from which the

[1] Germ. Pat. 160,046 (1904); Eng. and Min J. **84**, 673 (1907).

[2] Min. Ind. **22**, 875 (1913).

[3] Z. f. angew. Ch. p. 160 (1891); Chem. Zeitung, p. 1906 (1894).

[4] See Blount, *Practical Electrochemistry*, p. 81, footnote.

cathode compartment is separated by a diaphragm, and the remaining copper is oxidized to cupric chloride. The anode solution is then ready for treating the ore a second time. This process was also tried on a large scale, but seems to have failed largely on account of mechanical difficulties, especially with the diaphragm, and because of imperfect extraction of copper from the ore.

Another method of recovering copper from copper sulfate liquors has been worked out by Addicks,[1] based on the depolarizing action of ferrous sulfate using carbon anodes, the prevention of the solution of cathode copper by ferric sulfate by adding aluminum sulfate and thus avoiding the use of diaphragms, and the reduction of ferric sulfate by sulfur dioxide outside the cell room.

The largest plant in the world for the extraction of copper by leaching and electrolytic deposition is that of the Chili Exploration Company at Chuquicamata, Chili, which has recently been taken over by the Anaconda Copper Mining Company. Operations on a producing basis started May, 1915. The copper is chiefly in the form of basic sulfate (brochantite), but appreciable amounts of basic copper chloride (atacamite) and some nitrates are also present. The copper content of the oxidized ore body averages 1.91 percent. The main impurities to be considered are the chlorine and nitrates.

The ore is crushed to $\frac{3}{8}$ in. diameter (9 mm.) and is leached in dilute sulfuric acid in reënforced concrete tanks lined with mastic asphalt made by the Vulcanite Paving Company of Philadelphia. There are six leaching tanks 150 ft. long, 110 ft. wide, and $17\frac{1}{2}$ ft. deep (45.6 by 33.5 by 5.3 m.). These each hold 10,000 tons of ore. There are also three tanks of the same length and breadth, $19\frac{1}{2}$ ft. deep, each holding 12,000 tons. Six days are required for treating the ore : one to fill the tank, two for leaching, two for washing and draining, and one for discharging. The spent electrolyte returning from the electrolytic tanks serves as a second-treatment solution in the leaching process. The extraction obtained is slightly over 90 percent.

Before electrolyzing this solution the chlorine concentration has to be reduced to less than 0.5 g./l. For this purpose the solution is agitated with finely divided cement copper. The size of the copper plays an important part in this operation. The cuprous chloride formed is dissolved in ferrous chloride and the cement copper is recovered by passing this solution of cuprous copper over scrap iron.

[1] Tr. Am. Electroch. Soc. **28**, 73 (1915).

After removing the chlorine the leach solution is passed through electrolytic tanks where copper is deposited on pure copper starting sheets. The anodes were originally hollow magnetite castings with walls 6 mm. thick (0.24 in.). The outside dimensions were 13 cm. wide, 5 cm. thick, and 120 cm. long (5.1 by 2 by 47 in.). Five were placed on one bar. They were copper plated on the inside to give the requisite electric conductance. They were very fragile and the difficulty of getting a uniform copper plating on the insides of the casting did much to shorten their life. Duriron, which is the trade name for ferrosilicon containing 12 to 14 percent silicon, was substituted as anode material. Though this is not entirely unattackable and has more resistance than the magnetite electrode, it proved economically practical. More recently this has been superseded by a new alloy of copper, iron, and silicon, developed by the Chili Copper Company. One of the chief objections to the duriron anode was the amount of iron introduced into the solution, which had to be discarded with a simultaneous loss of acid. Lead anodes cannot be used on account of the nitrates present.

The electrolytic tanks, like the leaching tanks, are made of reënforced concrete and lined with mastic asphalt. Each tank is 5.7 m. long (19 ft.), 1.95 m. wide (3.5 ft.), and 1.5 m. deep (5 ft.). There are 894 tanks in all, 80 of which are used for starting sheets. They are arranged in eight electrical circuits and the solution flows through 16 in cascade. Starting sheets are deposited on copper blanks in special tanks with copper anodes. A relatively pure copper sulfate solution, entirely separate from the leach liquor, is circulated through these.

The tank lining tends to become plastic above 40° C., so in order to prevent the electrolyte from becoming too warm a portion of the partly electrolyzed solution is pumped back to the storage tank and mixed with the incoming solution in order to equalize the temperature over the tankhouse. These results are obtained by running the solution through the tankhouse in two stages and if necessary over a cooling tower between the first and second stage.

The solution first entering the depositing tanks contains from 3 to 5 percent copper and 2.5 to 3 percent sulfuric acid, while the spent electrolyte finally leaving the tank room has a little over 1 percent copper and from 7 to 8 percent free acid.

The starting sheets are approximately 3 ft. by 4 ft. The copper-silicon-iron anodes are in the form of slabs 1 in. by 5 in. wide by 52 in. long. Five of these are suspended 2 in. apart from a

copper bar. In connecting the cathodes of a tank to the anodes of the next tank the Whitehead V-notch contact is used in which the cathode bar in one tank rests on the anode lug in the adjacent tank.

With a current density of 12 to 14 amp./sq. ft. with duriron anodes a tank takes about 3 volts. The current efficiency is from 83 to 86 percent. Anode consumption is from 4 to 7 percent of copper deposited. Tanks with the copper-silicon-iron anodes take only 2.3 volts, and these anodes last much longer.

Cathodes are pulled every 8 or 10 days weighing 140 to 160 lb. They are sent directly to the oil-fired melting furnace, where they are refined and cast into high-grade wire bars.

The capacity of the plant is 20,000 tons of ore a day, corresponding to 9000 tons of wire-bar copper a month.[1]

Electrolytic Zinc Extraction. — The ordinary method of recovering zinc from its ores is to smelt in small externally heated retorts holding about 60 pounds of ore. These retorts last only from 20 to 40 days, and the loss of zinc by volatilization amounts to 25 percent or more. It is partly for these reasons that the electrolytic method has been developed. This consists in leaching the ore, purifying the solution, and depositing the zinc by electrolysis, with lead anodes. In spite of the crudeness of the smelting method, electrolytic extraction can compete with smelting only when either power or ore is very cheap. Copper has not a very large margin of profit when extracted by the electrolytic method, and zinc is worth only one third as much and takes twice the energy per unit weight to decompose from a solution of its sulfate. Another limitation of the electrolytic method is that not all ores can be leached by present methods.

During the last ten years a number of plants in this country have developed the electrolytic method of zinc extraction from ores, using sulfate solutions, which are preferred to chloride solutions because the cells are simpler. They require no covers for leading off chlorine or diaphragms for keeping chlorine from the cathodes, both of which are necessary with zinc chloride solutions. The largest of these plants is that of the Anaconda Copper Mining Company at Great Falls, Montana, which produces 150 tons of electrolytic zinc a day. In this plant a complex zinc sulfide ore is roasted, giving a mixture of zinc oxide and zinc sulfate. This

[1] The description of this plant is taken from E. A. Cappelen Smith, Tr. Am. Electroch. Soc. **25**, 193 (1914), and from recent information kindly furnished by Mr. H. C. Bellinger, Vice-President of the Chili Exploration Company.

ıs leached with a dilute solution of sulfuric acid. The recovery is only 70 to 80 percent of total or 95 to 98 percent of acid-soluble zinc. This solution is then purified in order to get a good zinc deposit. If purification is not properly done, zinc comes down in a spongy form which cannot be melted without large oxidation loss. ·

In order to prevent the formation of zinc sponge : (1) the solution must be very completely freed from all metals more positive than zinc, so that they will not deposit and by their lower overvoltage make the liberation of hydrogen more easy. This would not only cause less zinc to deposit but would cause a large amount of zinc to dissolve by local action ; (2) the solution must be slightly acid so that basic compounds of zinc will not be deposited on the cathode ; (3) the current density should not be below a certain minimum value, which may vary with other conditions but is about 1 amp./sq. dm.; (4) the concentration of zinc should be high, between 40 and 60 g./l.; and (5) the temperature should be kept low.[1]

The degree to which purification is necessary is shown below, where the maximum amounts of different impurities allowable are given if present alone in solution. If more than one are present, a smaller amount is allowable in each : [2]

	Mg./L.		Mg./L.
Copper	10	Iron	30
Antimony	1	Arsenic	1
Manganese	350	Cadmium	12
Chlorine, less than	50	Cobalt	1

Vanadium is even more harmful than cobalt. Impurities cause trouble : (1) by depositing with zinc and making it impure, as in the case of cadmium, (2) by interfering with the electrolysis, and (3) by trouble in filtering. Antimony and cobalt are the most harmful impurities for the electrolysis, causing rapid solution of the deposited zinc. Iron and silica cause trouble in filtering.

The solution entering the first tank of a cascade is nearly neutral and contains 6 to 8 percent zinc; on leaving the last tank it con-

[1] The following are some of the more important of the numerous investigations on sponge zinc: Kiliani, Berg- und Hüttenm. Ztg. 1883, p. 250; Nahnsen, Berg- und Hüttenm. Ztg. 1891, 393; Mylius and Fromm, Z. anorg. Ch. **9**, 164 (1895); Foerster and Guenther, Z. Elektroch. **5**, 20 (1898), and **6**, 301 (1899).

[2] Ralston, *Electrodeposition and Hydrometallurgy of Zinc*, p. 74 (1921). Somewhat different values are given for some of the impurities by Ellsworth, Tr. Am. Electroch. Soc. **42**, 63 (1922).

tains 0.8 to 4 percent zinc and 5 to 15 percent sulfuric acid. This solution is used again for leaching.

The electrolysis tanks of the Great Falls plant [1] are made of wood, lead lined, and are 3.12 m. (10 ft. 3 in.) long, 0.86 m. (2 ft. 10 in.) wide, and 1.5 m. (5 ft.) deep. The cathodes are of aluminum, 61 cm. wide by 107 cm. long by 0.48 cm. thick (2 ft. by 5 ft. by $\frac{3}{16}$ in.), 91 cm. (3 ft.) of which are submerged. The anodes are soft lead 0.95 cm. ($\frac{3}{8}$ in.) thick and 2.5 cm. (1 in.) smaller all around than the cathodes. There are 28 anodes and 27 cathodes per tank, placed with their adjacent surfaces 3 cm. ($1\frac{3}{4}$ in.) apart. The tanks are placed in cascades of six, but some fresh solution is added
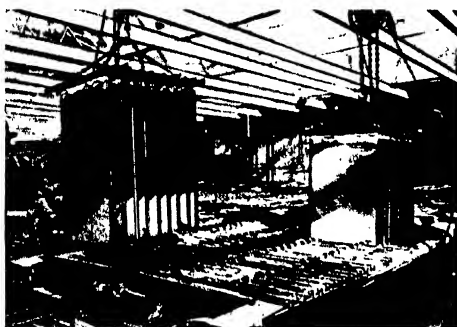
Courtesy Anaconda Copper Mining Company
FIG. 56. — DRAWING ZINC, GREAT FALLS ELECTROLYTIC ZINC PLANT

to each tank besides that from this circulation. 28 to 42 grams of glue per ton of metal produced are added at two-hour intervals.

The current per tank is 10,000 amperes and the current density is 3.2 amp./sq. dm. With 10 percent acid the voltage is 3.8. The tank house has 864 cells divided into six electrical units of blocks of 144 cells, subdivided into 24 cascades.

The cathodes, shown in Figure 56, are usually stripped every 48 hours and are 1 to 2 mm. thick, weighing 15 to 20 lb. The current efficiency is higher the higher the current density and the lower the acid concentration. If the acid concentration is increased, the current density must be increased correspondingly to keep the efficiency constant. The current efficiency may be 96

[1] Laist, Frick, Elton, and Caples, Tr. Am. Inst. Min. Met. Eng. **64,** 699 (1921).

to 98 percent at first but drops off as the acid concentration increases.[1]

The current density in practice lies between 1.1 and 2.7 amp./sq. dm., but very smooth dense zinc is obtained at 11 amp./sq. dm. with a solution containing 250 to 300 grams of free acid per liter.[2]

The temperature of the electrolyte is around 40° C. and this requires lead-pipe cooling coils usually placed at the outlet end of the tank.

The cathodes are melted by immersion in a bath of melted zinc and cast. The purity of cast zinc is 99.9 percent.[3] About 5 percent is lost as dross in melting. Ammonium chloride is used as a flux. One of the problems of the electrolytic process is to recover the zinc from dross.

The acid spray attacks the aluminum cathodes above the solution and causes a constant deterioration in that portion of the plates. With aluminum at 50 cents a pound this amounts to 75 cents per ton of zinc deposited. So far no coating has been found that will resist the acid for any length of time. The aluminum cathode is $\frac{1}{8}$ to $\frac{3}{8}$ in. thick. Plates $\frac{1}{4}$ in. thick do not stand stripping, as they become rough and peel off with the zinc.

Zinc was made from chloride solutions before sulfate solutions were used, but the only plant using zinc chloride made from roasted ore is that of Brunner, Mond and Company at Winnington, England, by a process worked out by Hoepfner.[4]

Electrolytic Gold Extraction. — Gold is extracted from ore containing as little as 8 grams per ton by stirring thoroughly with solutions containing 0.1 to 0.05 percent KCN.

The reactions taking place are : [5]

$$2 \text{ Au} + 4 \text{ KCN} + 2 \text{ H}_2\text{O} + \text{O}_2 = 2 \text{ KAu(CN)}_2 + 2 \text{ KOH} + \text{H}_2\text{O}_2,$$
$$2 \text{ Au} + 4 \text{ KCN} + \text{H}_2\text{O}_2 = 2 \text{ KAu(CN)}_2 + 2 \text{ KOH}.$$
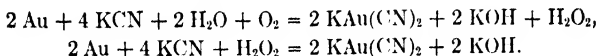
Sodium cyanide can also be used.

The gold is then recovered from the solution either by the MacArthur-Forrest method of precipitation by zinc or the Siemens and Halske process of electrolytic deposition.

[1] For tables of current efficiencies under different conditions, see Hansen, Tr. Am. Inst. Min. Eng. **60**, 206 (1918).

[2] Tainton, Tr. Am. Electroch. Soc. **41**, 389 (1922).

[3] *Copper*, published by the Anaconda Copper Mining Co. p. 45 (1920).

[4] See Guenther, *Die Darstellung des Zinks auf Elektrolytischem Wege* (1904).

[5] Bodlaender, Z. angew. Ch. for 1896, p. 583.

The *Siemens and Halske* process was first used in South Africa.[1] Iron anodes were used, 0.3 to 0.6 cm. thick, and lead-foil cathodes 0.00008 cm. thick. The anodes and cathodes were placed vertically 4 cm. apart. The sizes of the electrolysis tanks varied considerably. The first were 2.1 m. (6.2 ft.) long by 0.9 (2.9 ft.) wide, but in later installations the size was reduced to facilitate handling. The anodes were inclosed in textile material to prevent short circuits and to collect the Prussian blue and iron oxide formed from the anodes.

The lead cathodes were frequently cut into narrow strips to increase the surface. They were strung on wires held in light wooden frames. The most favored form of precipitating unit was to divide the containing box into alternate wide and narrow compartments. The narrow compartments served for the down flow of the solution, while the electrodes were suspended in the wide compartments, in which the solution has an upward flow. The current density was 0.0033 to 0.0066 amp./sq. dm. of anode surface. After the cathodes had received 2 to 12 percent of their weight of coherent gold deposit, they were removed and melted and the gold recovered by cupellation. At Minas Prietas, Mexico, new details were adopted as worked out by Butters. The tanks were 9 m. long, 3 m. wide, and 1.5 m. deep (29.6 by 9.9 by 4.9 ft.) with a sloping bottom for removing the precipitate. The arrangement of compartments was the same as in the Siemens and Halske process. Each wide compartment has 18 lead anodes 121 cm. by 56 cm., coated with lead peroxide by electrolyzing in a special cell.

There were 17 lead-foil cathodes cut in strips, as in the Siemens and Halske process, but were later changed to tin plate for increased mechanical strength. The current density was such that the metals were deposited as a flocculent precipitate which partly fell to the bottom of the cell, and partly adhered to the cathode. The current density was 0.059 amp./sq. dm. (0.55 amp./sq. ft.) of anode surface, at about 3 volts. The composition of the solution was as follows:

	GOLD, GRAMS PER TON	SILVER, GRAMS PER TON	CYANIDE IN TERMS OF KCN, PERCENT
Entering electrolysis cell . .	4.57	109.2	0.0792
Leaving electrolysis cell . .	0.404	9.02	0.0938

[1] Clevenger, Tr. Am. Electroch. Soc. **28**, 263 (1915). For an experimental study of the electrodeposition of gold and silver from cyanide solutions, see Christy, Bureau of Mines Bull. No. 150 (1919).

The percent precipitated was: gold, 91.0; silver, 91.7.

Of all anode material tried, peroxidized lead is the most satisfactory. An important advantage is that lead has a salvage value after serving as anode. Lead anodes are peroxidized in a cell where a few are treated at a time. At Minas Prietas they are first scratch-brushed and then electrolyzed in a 1 percent potassium permanganate solution with a current density of 0.11 amp./sq. dm. (1 amp./sq. ft.) for one hour. Fresh permanganate is added to keep the strength up to 1 percent.

At San Sebastian, Salvador, the peroxidizing electrolyte contained 1 percent of potassium permanganate, 2 percent sulfuric acid, and the current density was 0.28 amp./sq. dm. (2.6 amp./sq. ft.) for a period of 6 hours.

The life of peroxidized lead anodes is about 8 months to over a year.

The current efficiencies for the deposition of gold from solutions containing 10 grams of gold per ton and 0.05 percent potassium cyanide are:[1]

For current density = 0.25 amp./sq dm. (2.3 amp./sq. ft.) 7.6 percent
"   "   "   0.5 "   "   (4.6 "   ") 3.8   "
"   "   "   2.4 "   "   (22 "   ") 0.4   "

The electrolytic method is not used at present because the zinc method is less expensive.[2]

Electrolytic Cadmium Extraction. — Cadmium occurs only in small quantities in its ores, and its production is profitable only as a by-product. A plant for the electrolytic recovery of flue dust consisting mainly of zinc oxide, with the production of cadmium as a by-product, was operated until the armistice at Kennett, California, by the United States Smelting, Refining, and Mining Company. In purifying the zinc solution for electrolysis copper and cadmium are precipitated by zinc dust. This precipitate, having the appearance of black mud, is dissolved in dilute sulfuric acid leaving copper behind. Cadmium is precipitated on zinc sheets by cementation, and is dissolved in acid cadmium electrolyte. Iron and thallium are removed, and cadmium is precipitated on rotating aluminum cathodes, from which it is easily stripped. Its sulfide is used as a pigment, and in the metallic state it is used for low-melting-point alloys.[3]

[1] Neumann, Z. Elektroch. **12**, 569 (1906).
[2] Gowland, *The Metallurgy of the Non-ferrous Metals*, p. 325 (1921).
[3] Hanley, Chem. Met. Eng. **23**, 1257 (1920).

Experiments on electrolytic cadmium are now in progress at the Great Falls plant of the Anaconda Copper Mining Company.

Electrolytic Iron Extraction. — In this country the Eustis process for extracting iron and producing pure iron either as tubes or sheets is under development. This process is as follows:[1]

```
                 ┌─────────────────────────────┐
                 │      Leach with FeCl₃        │
                 │  2 FeCl₃ + FeS = 3 FeCl₂ + S │
                 └─────────────────────────────┘
```

$$Leach\ with\ FeCl_3$$
$$2\ FeCl_3 + FeS = 3\ FeCl_2 + S$$

Gangue

Solution of $FeCl_2$ and $CuCl_2$

Sulfur to Market

Cementation Tanks
$$CuCl_2 + Fe = FeCl_2 + Cu$$

Copper to Market

Electrolytic Cell
$$3\ FeCl_2 = 2\ FeCl_3 + Fe$$

Anode
$FeCl_3$ Solution

Cathode Iron
99.99 Percent Pure
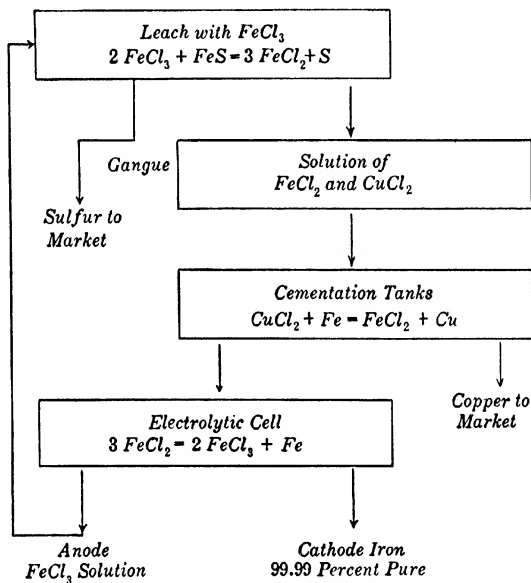
FIG. 57. — FLOW SHEET OF EUSTIS PROCESS

Pyrrhotite is leached with a solution equimolar in $FeCl_2$ and $FeCl_3$ according to the reaction:

$$FeS + 2\ FeCl_3\ =\ S + 3\ FeCl_2 + 22{,}000\ cal.$$

(700 B.t.u. per pound of iron dissolved).
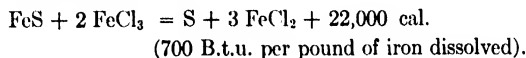
Sulfur and insoluble material are filtered off and the solution is purified. The sulfur is sold. Copper is removed by metallic

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[1] U. S. Pat. 1,377,822 (1921); Perin and Belcher, Mining and Metallurgy, No. 180, p. 17 (1921); Eustis, Mining and Met. Soc. of Am., Sept. 27 (1922); also Met. Chem. Eng. **27**, 684 (1920).

iron, zinc and cadmium by hydrogen sulfide or a soluble alkaline sulfide.

The flow sheet is shown in Figure 57.

The diaphragm cell used resembles a caustic soda cell. Iron is deposited from ferrous chloride solution on the cathode, and ferrous chloride is oxidized to the ferric state on graphite anodes in the anode compartment; the concentration of ferric chloride reaches 70 g./l. and about the same amount of ferrous chloride. The cathode current efficiency is 95 percent.

The purity of the iron causes it to be very ductile, rust resisting, and to have relatively high thermal and electrical conductivities.[1] Similar work is being done by the Consolidated Mining & Smelting Co. at Trail, B. C.

Electrolytic Nickel Extraction. — For a number of years nickel and copper were extracted by the Canadian Copper Company from ore containing 2 percent of each metal by a process due to David H. Browne, which was operated in Cleveland, producing daily 454 kg. of pure nickel and a corresponding amount of copper.[2]

The ore is roasted, and then reduced by coke in the presence of lime. There results a matte containing 20 to 25 percent copper, 18 to 23 percent nickel, 25 to 35 percent iron, and 26 to 33 percent sulfur. The matte is broken up into pieces about 1 mm. in diameter and freed from sulfur by roasting, after which it is reduced with charcoal, and half of the copper-nickel alloy poured into water to get it into a fine state of division so that it will dissolve easily. The other half is cast into anodes, 75 cm. wide, 60 cm. long, and 2.5 cm. thick, containing 53.4 percent copper, 43.08 percent nickel, and the rest iron and sulfur. A solution containing sodium chloride and hydrochloric acid flows over the finely divided nickel-copper and alloy in a shot tower in the presence of chlorine gas. This solution coming from the shot tower and containing 44.3 g. copper, 55.6 g. nickel, and 100 g. sodium chloride per liter passes to the electrolytic tanks in which copper is deposited. These are arranged in the multiple system, with the nickel-copper anodes described above, and with copper starting sheets as cathodes, which are removed for melting every three or four weeks. The anode scrap is remelted. The tanks are cement 256 cm. long, 85 cm. wide, and 67.5 cm. deep, and contain 1.534 cubic meters of electrolyte. The circulation is the cascade system. The voltage per tank is 0.25 to 0.41 volt and the current 500 amperes.

[1] Stoughton, Chem. Met. Eng. **16**, 128 (1922).
[2] Haber, Z. Electroch. **9**, 392 (1903).

Copper deposits in a coherent but not dense form, since the copper is deposited from a cuprous chloride solution. The current efficiency is between 85 and 95 percent. The solution from these tanks contains nickel and copper in the ratio of 80 to 1. The copper still remaining is removed by treatment with sodium sulfide and the copper sulfide is filtered off. Iron is then oxidized to the ferric state by chlorine from the nickel electrolysis baths and is precipitated by sodium hydrate. The solution is then concentrated in an evaporator for the precipitation of sodium chloride, after which the hot solution passes to the cells for electrolytic deposition of nickel.

The cells for nickel deposition are also of concrete, the circulation is in cascade, and the electrodes are connected in the multiple system. The dimensions are: 2.37 cm. long, 71.5 cm. wide, and 40 cm. deep. The cathodes are starting sheets of thin strips of sheet nickel 38 cm. long and 14.5 cm. wide. A number of these are hung on a rod placed lengthwise across the top of the tank. The anodes are graphite plates surrounded by a diaphragm consisting of clay cells of elliptical shape with the bottoms removed. These reach nearly to the bottom of the cells. Connection is made at the top of these diaphragms for carrying off the chlorine. The current efficiency for nickel is about 93.5 percent. The voltage is 3.6 for each bath with 896 amperes. The nickel cathodes are 3 cm. thick when finished, while the thickness of the starting sheets is 1 mm. The nickel is 99.85 percent pure, with 0.085 percent iron and 0.014 percent copper.

The *Hybinette* process is another method for extracting copper and nickel and separation of the two metals. It was first used in Norway and later at the Sault St. Marie works of the British America Nickel Corporation, Ltd., formerly the Canadian Nickel Company.[1] The bessemerized matte (known as " white metal ") contains 47 percent nickel, 32 to 34 percent copper, 20 percent sulfur, and 0.24 to 0.4 percent iron. This is granulated and is roasted to remove the bulk of the sulfur; it is then leached with 10 percent sulfuric acid, dissolving a large proportion of the copper and a very little nickel. The residue, containing 65 percent nickel, 3 to 8 percent sulfur, the rest copper with a trace of iron, is cast into anodes 91.5 cm. by 106.5 cm. and nearly 1.27 cm. thick. The cathodes are thin greased sheets of copper inclosed in porous bags, and have a wooden strip at the lower edge to pre-

[1] Report of the Royal Ontario Nickel Commission, p. 477 (1917); Kershaw, *Electrometallurgy*, p. 238 (1908).

vent buckling, as shown in Figure 58. The electrolyte, containing 45 g. of nickel and 3 to 5 mg. of copper per liter, is fed to the cathode compartment, where the level is kept higher than in the anode compartment to counteract the migration of copper. Thus only nickel is deposited, and this is stripped from the cathode sheets. The solution flowing from the anode compartment contains 2 to 3 g. of copper per liter, and is passed over anode scrap to cement the copper and enrich the solution in nickel. The solution is then sent back to the cathode compartment. The anode scrap amounts to about 30 to 40 percent of the original weight of the anodes and is about enough for this cementation. Each tank takes 3 to 4 volts, and the current density is from

FIG. 58. HYBINETTE PROCESS, ELECTROLYTIC DEPOSITION OF NICKEL

0.86 to 1.07 amp./sq. dm. (8 to 10 amp./sq. ft.). The cathodes are stripped every ten days, giving sheets 9.1 to 13.6 kg. in weight (20 to 30 lb.) and about 0.32 cm. thick. They are washed in sulfuric acid to remove basic salts and are cut into pieces 5 by 7.5 cm. for sale. The metal is guaranteed as follows:[1]

	PERCENT
Nickel (including up to 1 percent Co)	98.50
Iron, not more than	0.60
Copper, not more than	0.15
Sulfur, not more than	0.02
Carbon, not more than	0.02

The slime contains the precious metals.

The cement copper made by purifying the solution over the anode scrap is sent to the smelter to be cast into anodes for electrolytic refining.

The British America Nickel Corporation has also acquired the Madsden process for the manufacture of malleable electrolytic nickel sheet, plates, and tubes. This consists in lifting the cathodes periodically from the nickel bath and keeping them out a proper time, and then continuing the electrolysis.[2]

Electrolytic Extraction of Other Metals. — Manganese can be deposited if the anode and cathode are separated by a dia-

[1] From pamphlet published by the British America Nickel Corporation, Ltd., Ottawa, Canada.

[2] C. P. Madsden, Tr. Am. Electroch. Soc. **39**, 483 (1921).

phragm, and a 6- to 7-normal manganese chloride solution, 1.5 normal in ammonium chloride and 0.1 normal in hydrochloric acid is electrolyzed in the cathode compartment, with strong circulation, at a current density of 20 amp./sq. dm. at 30° C. The current efficiency is 50 to 60 percent. The purity is 99.9 to 100 percent. The manganese can be stripped from a copper cathode in the form of a sheet.[1]

Sulfate solutions do not seem to be so successful for metallic manganese.[2]

Chromium could be extracted by the electrolysis of the chromic acid solution given under the heading of electroplating, using a chromic acid solution containing a little chromium sulfate. This would be expensive, for chromium costs about $3 a pound in the form of 80 percent chromic acid, while it is only 12 cents a pound as 60 percent ferrochromium containing 4 to 6 percent carbon. A solution which gives a brittle but smooth deposit is the following:[3] 12 percent chromium sulfate, 13 percent chromic acid (CrO_3), and 11 percent chromium oxide. The chromic acid dissolves the oxide. It is not stated in the patents how the bath is to be kept up to strength or which of the compounds is decomposed.

Thallium can be extracted by the electrolysis of a nearly saturated solution of its sulfate, with a platinum anode and copper cathode with a current density of 1.5 amp./sq. dm. The deposit is in the form of flakes and needles.[4]

Indium can be deposited easily from solutions of its salts.[5]

Gallium can be deposited from its solution in sodium hydrate[6] or from a slightly acid sulfate solution.[7]

The Electrolytic Refining of Metals

General Principles. — The object of electrolytic refining is to purify the metal and to recover any valuable impurities it may contain.

[1] Unpublished work by Grube in Foerster, *Elektrochemie wasseriger Lösungen*, p. 580 (1922).

[2] Van Arsdale and Maier, Tr. Am. Electroch. Soc. **33**, 109 (1918).

[3] Salzer, Germ. Pat. 221,472 (1907); 225,769 (1909).

[4] Foerster, Z. anorg. Ch. **15**, 71 (1897); Zerber, Z. Elektroch. **18**, 619 (1912).

[5] Thiel, B. B. **37**, 175 (1904).

[6] Boisbaudran and Jungfleisch, C. r. **86**, 475 (1878); Uslar and Browning, Am. J. Sci. **42**, 389 (1916).

[7] Richards and Boyer, J. Am. Ch. Soc. **41**, 133 (1919).

The process consists in electrolyzing the impure metal as anode in a solution of one of its salts, and depositing the pure metal on a pure thin sheet of the same metal, known as a *starting sheet*. In some cases the cathode consists of a different metal, from which the deposited metal is stripped as thin sheets, or as loose crystals. Where starting sheets are used, the deposited metal is not removed, but both are melted down into the required form for shipping.

The impurities are separated both at the anode and at the cathode. Impurities consisting of metals which are precipitated from their solutions by the metal to be refined (that is, more electropositive metals) do not dissolve appreciably, but either stick to the anode or drop off and form a part of the substance that collects in refining tanks, and which is known as *anode mud* or *anode slime*. The metals that would precipitate the metal to be refined from its solution, or which are more electronegative dissolve, and remain in solution unless an insoluble compound is formed. In this case even a more electronegative metal may be found in the slime.

Since the impurities which are in solution are more electronegative than the metal to be refined, they are not deposited at the cathode. The electropositive metals are therefore separated at the anode, the electronegative at the cathode. Any metal which has nearly the same electrolytic potential as the metal which is refining can be separated from it only imperfectly.

The soluble impurities would increase in concentration in the solution and might finally become so concentrated that they would be deposited on the cathode. For this reason the solution must be purified from time to time. This is done by taking a certain portion of the solution from the tanks for purification continuously and replacing by pure solution.

Precious metals are electropositive to others, and are therefore found in the slimes. An important part of metal refining therefore consists in working up the slimes to recover and purify these metals. This may involve one or more further electrolytic treatments similar to the one by which the original slime was produced. Thus in copper refining, silver, obtained from the slime containing gold and platinum, may be cast into an anode and the silver refined. This gives anode mud containing gold and platinum. The gold-containing platinum is then refined, but in this case the platinum goes into solution and is separated from the gold at the cathode.

Electrolytic Copper Refining. — Copper of high purity is required for the construction of electric machinery, on account of the better electric conductivity of pure copper. Moreover, the impurities in copper usually consist of one or more precious metals, such as silver, gold, and platinum, besides others of less value, which can be recovered by refining. For these reasons the electrolytic refining of copper is one of the largest of the electrochemical industries. The United States furnishes over one half of the world's copper, 81 percent of which is electrolytic.

Table 33 gives a list of the principal electrolytic copper refineries of North America with their yearly capacity in pounds.

TABLE 33. ELECTROLYTIC COPPER REFINERIES IN NORTH AMERICA [1]

WORKS	LOCATION	YEARLY CAPACITY IN POUNDS	PROCESS
American Smelting & Refining Co.	Baltimore, Md.	720,000,000	Series and Multiple
Nichols Copper Co.	Laurel Hill, N. Y.	500,000,000	Series
Raritan Copper Works	Perth Amboy, N. J.	480,000,000	Multiple
U. S. Metals Refining Co.	Cartaret, N. J.	240,000,000[2]	Multiple
American Smelting & Refining Co.	Maurer, N. J.	240,000,000	Multiple
Anaconda Copper Mining Co.	Great Falls, Montana	216,000,000	Multiple
American Smelting & Refining Co.	Tacoma, Washington	204,000,000	Multiple
Calumet & Hecla Mining Co.	Hubbell, Mich.	60,000,000	Multiple
Consolidated Mining and Smelting Co.	Trail, B. C.	50,000,000	Multiple
British America Nickel Corp.	Deschenes, Que.	8,000,000	Multiple
		2,718,000,000	

The Electrolyte. — The electrolyte consists of a copper sulfate solution containing free sulfuric acid and 1 to 2 parts of glue are added to 8,000,000 parts of electrolyte every day. The additions are made in 8- to 12-hour intervals. Glue toughens the deposit and if too much is used, it will cause sharp needle-like crystals to form on the points of the nodules and also causes the nodules to adhere very tenaciously to the cathode. This gives a rough cathode and low current efficiency.

[1] Yearbook of the Am. Bureau of Metal Statistics for 1922, p. 17.
[2] Now being increased 50 percent.

In the tanks for making starting sheets a larger amount of glue is used, from 1 to 2 parts to 150,000 of solution. This is to give the sheet the necessary toughness so it can be stripped easily. This extra amount of glue increases the resistance of the electrolyte 5 percent.

The electrolyte also contains a small amount of sodium chloride or hydrochloric acid to precipitate antimony as the oxichloride. The chlorine concentration is generally maintained at from 0.035 to 0.050 g./l. Too much salt will cause needles or moss to form on the cathodes.

The composition of the solution has gradually been changed from 4 percent copper and 8 percent free acid to the present values of 2.75 percent copper and 12 percent free acid.[1]

The composition tends to change during working on account of the solution of electronegative impurities in place of an equivalent amount of copper. On the other hand, copper dissolves in sulfuric acid under the influence of atmospheric oxygen. In the case of high-grade anodes, chemical solution of copper more than makes up for the loss due to impurities, and about 1 to 2 percent of the cathode capacity has to be removed either by crystallizing copper sulfate or by depositing the copper with unattackable anodes often consisting of antimonial lead.

The temperature of the electrolyte should be near the practical limit of 60° C., and is heated in storage tanks by steampipes. The main reason for using a warm electrolyte is that it makes the deposited copper smoother and denser, makes the use of higher current densities possible, and lowers the power required, but it also increases the chemical action. With no steam heating and with a current density of about 1.7 amp./sq. dm. (16 amp./sq. ft.), the temperature of the electrolyte would be about 14° C. above the temperature of the atmosphere of a tank room, which is around 21° C. and it is very humid unless there is good ventilation.[2]

Continuous circulation is necessary to equalize the differences in composition caused by the electrolysis. The solution tends to become concentrated at the anode and dilute at the cathode, and if left to itself, the heavy solution would fall to the bottom of the tank and the light solution would rise to the top. This would result in a very uneven deposit of copper, for the concentrated

[1] Addicks, *Copper Refining*, p. 52 (1921).
[2] Addicks, Met. Chem. Eng. **16**, 311 (1917); and *Copper Refining*, p. 60 (1921).

solution at the bottom would conduct better, and cause a heavier deposit of copper on the lower end of the cathode than elsewhere. The anodes would also be unevenly attacked. The greater the current density the greater the rate of circulation must be, but it must not be so rapid as to prevent the settling of the anode mud. For 20 amp./sq. ft. the rate is $3\frac{1}{2}$ gal./min. At this rate the solution in a tank 11 ft. by $3\frac{1}{2}$ ft. by $3\frac{1}{2}$ ft. would be replaced in 3 to 4 hours.

The usual method of circulation is to arrange rows of vats on terraces with steps 5 to 8 centimeters high (2 to 3 in.) and to allow the solution to overflow from the higher to the lower rows of tanks. The electrolyte is collected in a well from which it is raised by a pump to a main, whence part flows to a distributing box for the tanks, and part goes to vats with insoluble anodes where the electrolyte is freed from dissolved metals and is then returned to the main circuit. A partition at the end of each vat reaches to within 15 to 20 centimeters of the bottom. The overflow is thus received at the top and drawn from the bottom, or the reverse. It is preferable to have the solution leave by an overflow at the top, as this maintains a more uniform level of solution. A uniform level is essential, as a changing level tends to dissolve the cathode and cut it off entirely. Also an overflow from the bottom offers more chance for the slime to be carried to the launders and heating tanks.

Circulation does not entirely prevent stratification. This is evident from the table on the following page showing the condition at Great Falls, where the current density has the high value of 3.9 amp./sq. dm. (36 amp./sq. ft.) The samples of electrolyte were taken between the center pair of electrodes at the distances below the surface of the electrolyte shown in the first column.[1]

The simplest and the original method of purifying the electrolyte consists in cementing the copper upon iron and throwing the copper-free liquor away. Scrap iron is piled in a lead-lined tank, the liquor run in and brought to boiling by steam heat, and precipitation is complete in an hour. The copper-free liquor is run into the sewer and an occasional cleaning of cement copper is made. Sometimes more than twice the theoretical weight of iron is required for precipitating the copper, on account of the fact that the iron is not pure, some is dissolved by the free acid, and other metals besides copper are precipitated.

This method is simple, but the copper is only about 70 percent

[1] Burns, Trans. Am. Inst. Mining Eng. **46**, 703 (1913).

CIRCULATION AT THE RATE OF 23 LITERS PER MINUTE

DISTANCE BELOW SURFACE	SPECIFIC GRAVITY	ACID, IN GRAMS PER LITER	COPPER, IN GRAMS PER LITER
15 cm.	1.213	174	38.4
100 cm.	1.228	153	49.9

CIRCULATION AT THE RATE OF 57 LITERS PER MINUTE

15 cm.	1.210	167	37.8
100 cm.	1.265	146	66.4

CIRCULATION SHUT OFF SEVEN HOURS

15 cm.	1.185	179	23.4
100 cm.	1.255	138	65.5

pure, the scrap iron is a large item of expense, and both free and combined sulfuric acid is entirely wasted. It is considered a legitimate emergency measure for dealing with a bad electrolyte.

The next purification method developed is to manufacture copper sulfate from electrolyte as raw material. The process is: (1) neutralization of free acid by anode copper, (2) concentration of neutral liquor by boiling, (3) crystallization of heavy liquor, and (4) cementation of mother liquor. The plant required is large, and is dependent on the market for blue stone. This method is still more or less used, though generally in addition to other methods.

The method of purification in general use is to divert to insoluble anode tanks just enough electrolytes to keep the determining impurity at the desired point. This is either nickel or arsenic, and is usually nickel.[1] If arsenic is the main impurity and but little nickel is present, the solution may be returned directly to the refining tanks after plating out all of the arsenic and copper. Three tanks in series are required to reduce the copper and arsenic down to 0.1 percent or less. If much nickel is present, the liquor is sent to a steam boiling tank in place of being returned to the refining tanks, where it is concentrated to a specific gravity of 1.37 (40° Beaumé). The liquor is now nearly copper free, and of high acid content, consequently not seriously corrosive, and is transferred to a boiler-plate tank, where it is concentrated by direct fire to a

[1] Addicks, Met. Chem. Eng. 16, 689 (1917).

specific gravity of 1.91 (66° Beaumé). At this strength all impurities have been precipitated as anhydrous sulfates except the small amount of arsenic which came through the insoluble anode tanks and the sodium and potassium salts. The heavy liquor is separated from its suspended solids by a sand filter. The salts
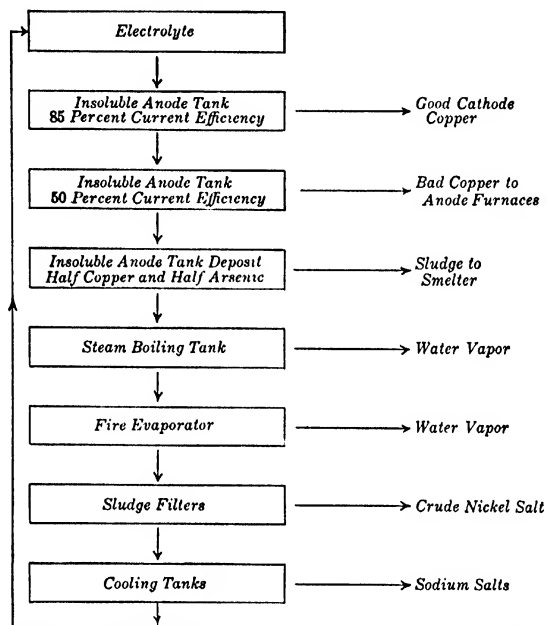
FIG. 59. — FLOW SHEET, PURIFICATION OF ELECTROLYTE IN COPPER
REFINING

are transferred to a draining board, and then to a sucking tub, where the remaining acid is washed out with a little water. The partly washed salts are then shoveled on to a drying floor. The strongly acid filtrate is chilled, with the consequent precipitation of much of the sodium sulfate, and is then returned to the main electrolyte.

The process is illustrated by the flow-sheet in Figure 59.[1]

It has been proposed to take advantage of the tendency of the

[1] Met. Chem. Eng. **16**, 691 (1917).

solution to stratify to effect a saving in the number of tanks with unattackable anodes.[1] The plan is to eliminate the first series of tanks with unattackable anodes, by allowing the solution to stratify in tanks especially designed for the purpose, so that a solution can be obtained whose copper content is the same as that entering the second set of tanks with unattackable anodes. The impurities do not stratify, so just as much impurity from the stratifying tanks per unit volume is removed as from the ordinary tanks.

A sectional elevation of a stratifying tank is shown in Figure 60. AB is the slime line, H the outlet for removing slime, CD the solu-

H Fig. 60. — Pyne's Stratifying Tank
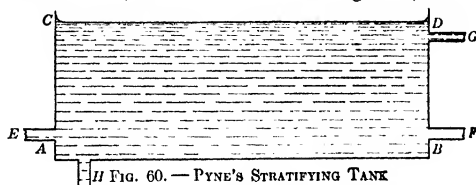
tion line. The electrodes are omitted for clearness. The electrolyte enters through E and is withdrawn through G and F. The flow from the upper and lower outlets is so regulated that there is sufficient copper in solution at all points of the cathode to give a good deposit, and still a solution high in copper is withdrawn from F, and a solution from G which is lower in copper than is usually obtained from the first set of tanks with insoluble anodes. The cathode is in all respects similar to those drawn from the regular refining tanks. Thus the first set of tanks with insoluble anodes may be omitted, with saving in the expense of depositing a large amount of copper with unattackable anodes.

Table 34 gives the analysis of a representative electrolyte.

TABLE 34. ANALYSIS OF REPRESENTATIVE ELECTROLYTE [2]

Specific gravity, 1.226
Free acid, 12.03 percent

	PERCENT		PERCENT
Copper	2.94	Bismuth	0.0026
Nickel	1.48	Zinc	0.0166
Chloride	0.0031	Alumina	0.0595
Arsenic	0.916	Calcium sulfate	0.1384
Antimony	0.0350	Magnesium sulfate	0.0370
Iron	0.060	Sodium sulfate	0.5048

[1] Pyne, Tr. Am. Electroch Soc. **28**, 111 (1915).
[2] Addicks, Met. Chem. Eng. **16**, 689 (1917).

The working resistance of the electrolyte at 49° C. is about 2.0 ohms per centimeter cube (0.8 ohm per inch cube).[1] If these results in the foot-note are represented graphically, they show that the addition of copper sulfate to a sulfuric acid solution containing 3 g. of acid per 100 cc. does not change the conductivity; for more dilute acid the conductivity is increased, and for more concentrated, it is reduced. The temperature coefficient for solutions containing equal amounts of sulfuric acid and anhydrous copper sulfate is about 0.97 percent per degree.

The Composition of Anodes and Cathodes. — The composition of anodes and cathodes is given in Table 35.[2]

TABLE 35. AVERAGE COMPOSITION OF ANODES AND
OF CATHODES AFTER MELTING TO WIRE BARS

ELEMENT	PERCENT IN ANODE	PERCENT IN WIRE BAR	PERCENT OF ORIGINAL IMPURITY IN ANODE FOUND IN WIRE BAR = A	EFFICIENCY OF REFINING = 100 − A
Copper . . .	99.030	99.939		
Silver . . .	0.1687	0.00131	0 78	99.22
Gold	0.0051	0.000013	0.25	99 75
Sulfur . . .	0.0075	0.0029	38.60	61.40
Nickel . . .	0.3200	0.0037	1.15	98.85
Lead	0.0567	0.0020	3.52	96.48
Arsenic . . .	0.0523	0.0015	2.87	97.13
Antimony . .	0.0409	0.0034	8.32	91.68
Bismuth . .	0.0051	Trace	———	———
Tellurium . .	0.0282	0.00015	0.53	99.47
Selenium . .	0.0682	0.00040	0 59	99.41
Iron	0.0181	0.0039	31 55	78.45

The electrical conductivity, annealed, is 100 to 101 percent of the Annealed Copper Standard (100 percent corresponds to 0.15328 ohm per metergram at 20° C.).

This table shows that while measurable amounts of practically all impurities are found in the cathode, the efficiency of refining is very high for most of the impurities. The poor showing of iron and sulfur is due to the introduction of these impurities in melting.

[1] Addicks, *Copper Refining,* p. 52 (1921). For conductivities of mixtures of copper sulfate and sulfuric acid in different proportions see Richardson and Taylor, Tr. Am. Electroch. Soc **20,** 179 (1911); Goodwin and Horsch, Chem. and Met. Eng. **21,** 181 (1919); Kern and Chang, Tr. Am. Electroch. Soc. **41,** 181 (1922).

[2] Addicks, Met. Chem. Eng. **16,** 688 (1917).

The impurities in the finished cathodes are guaranteed not to exceed 0.12 percent, and the copper commonly does run 99.93 percent in the melted bar. The impurities in the cathode may get there in a variety of ways:[1] by electrolytic deposition, by inclusion in the crystalline structure of the cathode, mechanical contamination from anode slimes suspended in the electrolyte, and substances entering during melting from the furnace, fuel, or tools. The relative extent to which these sources are responsible for the impurities in the cathode has not been determined. Impurities may cause a lowering in the conductivity, as with phosphorus, aluminum, silicon, arsenic, and antimony; or they cause brittleness or weakness, as with bismuth, lead, tellurium, and selenium, or they may be a source of loss of valuable by-products, as in the case of silver, gold, platinum, and palladium.

The metallic impurities in cathode copper may total 0.02 percent, having an unaccounted-for difference, part of which is supposed to be included electrolyte and part hydrogen either occluded or as hydride.[2]

TABLE 36.   ANALYSES OF TYPICAL ANODE SLIMES [3]

| | PERCENT RAW | | | PERCENT BOILED | |
	A	B [4]	C	D	E
Copper	14 3	43.3	20	1 60	1.14
Silver	35.0	17.2	37	11 5	29.5
Gold	0.64	0.12	0 6	0.7	0.7
Platinum	---	0.00017	...	0.0007	---
Palladium	---	---	...	0.0006	---
Nickel	5.25	0.08	.	0.89	1.07
Cobalt	---	0.006	..	...	---
Arsenic	2.68	3.03	4.0	1.42	1.20
Antimony	5.35	3.46	8.0	3.84	5.70
Bismuth	0.46	0.11	..	0.37	0.20
Sulfur	1.69	13.21	---	2.48	1.97
Iron	0.17	0.36	---	0.24	0.26
Lead	2.44	0.76	---	7.33	18.60
Selenium	5.70	1 20	---	12.94	11.24
Tellurium	2.69	2.10	---	5 72	6.20
Zinc	Trace	0.09	---	Trace	Trace
Silica	4.40	0.18	.	5.29	4.71

[1] Addicks, Tr. Am. Electroch. Soc. 26, 51 (1914); Met. Chem. Eng. 16, 687 (1917).

[2] Addicks, Met. Chem. Eng. 16, 24 (1917).

[3] Addicks, Met. Chem. Eng. 17, 171 (1917)

[4] Burns, Tr. Am. Inst. Min. Eng. 46, 712 (1913).

The Anode Mud. — The anode mud amounts to *1 to 3 percent* of the anode after coarse particles have been removed by passing through a 40-mesh screen (containing holes 0.062 cm. square). When this has accumulated in sufficient quantity, after a week or ten days, the tanks are cut out of service, and the electrodes removed. The solution is allowed to clarify for an hour and is drawn off; the slime is then sluiced out through a hole in the bottom of the tank with a trough leading to the collecting tank. Table 36 gives the analyses of typical anode slimes.

Slime B is from converter anodes, giving high copper and sulfur contents. C and D are analyses after the slime has been somewhat oxidized and leached with dilute sulfuric acid to remove the copper.

The problem of working up slimes is the most difficult of all in copper refining.[1] It consists in (1) the production of nearly copper-free slime, by screening the coarse copper and dissolving the rest with boiling sulfuric acid in the presence of air or a nitrate; (2) smelting to doré, which is silver containing gold and the other impurities, and (3) refining the silver and gold, usually electrolytically. The bullion is cast into anodes and refined electrolytically.

The large amount of copper in the slimes comes from the large pieces that fall from the electrodes, and from the fact that part of the copper dissolves in the univalent state, and then changes according to the reaction:

$$2\,Cu^+ = Cu + Cu^{++},$$
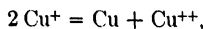
thus depositing finely divided copper. (See page 134.)

The by-products of electrolytic copper refining are the following: gold, silver, platinum, palladium, lead, nickel, and antimony, which have an unlimited market: bismuth, arsenic, cobalt, and selenium, with a limited market; and tellurium, with no market at all.[2] Both selenium and tellurium could be produced in large quantities if there were a sufficient demand.

The Behavior of Impurities in Copper Anodes.[3] — The impurities in copper anodes to be considered are:

[1] Addicks, *Copper Refining*, p. 108 (1921), where details of the present practice are given.

[2] Addicks, Met. Chem. Eng. **17**, 169 (1917).

[3] Hofman, *Metallurgy of Copper*, p. 485 (1914); Kiliani, Berg. und Hüttenm. Ztg., 1885, 249, 261, and 273. The presence of Ag_2Se and the compounds subsequent to this under group 3 from private communication.

1. Mn, Zn, Fe, Co, Ni, Sn, Pb, electronegative to copper.
2. Ag, Au, Pt, Se, Te, electropositive to copper.
3. Cu_2O, Cu_2Se, Cu_2Te, Cu_2S, Ag_2Se, Ag_2Te, possibly also arsenates of Bi and Sb.
4. As, Bi, Sb.

The metals of the first group are more electronegative than copper and are therefore completely converted to sulfates. Manganese, zinc, iron, cobalt, and nickel are also attacked by free acid and neutralize it. The sulfates of these metals are soluble and consequently accumulate in solution and must be removed from time to time as explained above. They can become fairly concentrated before there is danger of their deposition on the cathode with the copper, because they are so much more electronegative than copper.

Iron dissolves as ferrous sulfate, and is then oxidized to ferric sulfate by the current and the air. On reaching the cathode by circulation it will then be reduced to ferrous sulfate, causing a lowering in the current efficiency for copper.

Lead sulfate is insoluble and goes into the anode mud.

Tin first dissolves and then is precipitated as a basic sulfate, but if much is present in the anodes, the greater part will be left as a basic sulfate on the anode itself.

The metals of the second group all go into the anode mud, though if the solution were neutral, silver would dissolve and be precipitated with the copper.

None of the metals of the third group are attacked electrolytically. Cuprous oxide, which is always present in copper anodes, falls to the bottom and is slowly dissolved by the acid.

The fourth group consists of metals that go partly into the mud, and partly into solution, and this group causes the greatest difficulties in copper refining.

Arsenic probably first forms arsenic sulfate, but this is nearly completely hydrolyzed :

$$As_2(SO_4)_3 + 3\,H_2O = As_2O_3 + 3\,H_2SO_4.$$
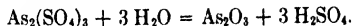
The arsenic oxide is partly precipitated and goes into the mud, while a certain part stays in solution, corresponding to its solubility. If nickel is present in the anode, it forms an insoluble alloy with arsenic, and causes it to go nearly entirely into the mud.[1] If the arsenic content of the electrolyte reaches 2 percent,

[1] Min. Ind., 1912, p. 290.

it is precipitated on the cathode, and the aim is to keep it below 1.25 per cent. When only small quantities of arsenic are in the anode, it all goes into the mud.

The presence of small amounts of sodium chloride hinders the deposition of arsenic and antimony.

The behavior of antimony is similar to that of arsenic, going partly into solution and part remaining as basic sulfate on the anode. Part that dissolves separates on long standing. In large-scale work some insoluble dark compound of antimony is often seen floating on the surface of the electrolyte. There is then danger of its getting into the cathode. It is removed from the last series of vats by placing a screen across the outlet. The antimony content of the electrolyte appears to remain at about 0.03 percent. If the electrolyte is allowed to cool, antimony separates out as a grayish white basic salt on the side of the tanks and in the circulation pipes. At times this becomes a serious problem from the point of view of clogged pipes and launders.

Bismuth goes partly into the slime and partly into solution, but it separates in the course of time almost completely from the solution in the form of basic salts. Both bismuth and antimony usually occur in quantities too small to cause any trouble with cathode copper.

The Two Systems. — There are two methods of arranging the electrodes in the refining tanks, known as the *multiple system* and the *series system*. In the multiple system the electrodes are alternately anodes and cathodes, and all of the same kind are connected electrically. In the series system, only one electrode at each end of the tank is connected to the generator, and all the other electrodes are *intermediate* electrodes, that is, act as cathode on one side and anode on the other. They are all alike and consist of the impure copper. In order to separate the pure copper deposited on the cathode side of the intermediate electrodes from any undissolved impure copper on the other side, the cathode side of the electrodes is painted over with some material which is conducting but which makes mechanical separation possible, such as a solution of resin in alcohol.

The multiple system is much more extensively used than the series system and will be taken up first.

The Multiple System. — In the multiple system the tanks are made of wood and are lined with hard lead about $\frac{1}{8}$ in. thick, containing 6 percent antimony. The lining extends over the edges of the sides to prevent the wood from absorbing the elec-

trolyte.   A strip of some insulating material, such as maple, must
be placed on the lead-covered edge of the tanks on which to rest
the electrodes.

It has been found most economical in the long run to use high-
grade, long-leaf yellow pine lumber, selected for plenty of pitch,
for constructing the electrolytic tanks.   It should be thoroughly
dry to minimize shrinking.   In order to preserve the lumber it
should be painted with a number of coats of nonconducting asphalt
paint, rather than with a paint with a carbon base.   With ordinary
care and frequent painting the life of a tank is from 7 to 10 years.
After such an installation has been put into service it is essential
to repair leaks as fast as they develop, for although lead is resistant
to sulfuric acid, it is attacked by the organic acids formed when
sulfuric acid is brought in contact with wood, and the lining, as
well as the wood, is destroyed.   The tanks are supported on con-
crete or brick piers 9 or 10 feet high, for the easy detection of leaks
and run-overs.   Sometimes a block of granite is used as an acid-
proof footing for the piers.   These piers are built on an acid-
proof floor which drains toward lead-lined sump tanks.   Each
pier has a plate of glass between it and the tank to improve the
insulation,[1] as shown in Figure 63.   It has been found advisable
to place thin lead caps over the tops of the glass plates to protect
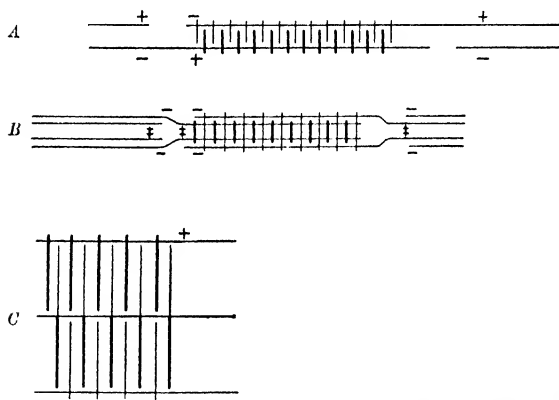
FIG. 61. — EVOLUTION OF CONNECTING TANKS IN THE MULTIPLE SYSTEM

[1] Easterbrooks, Met. Chem. Eng. 6, 245 (1908).

them from solution leaks, dust, etc., which reduce their insulating value.

The evolution of the method of connecting tanks together is shown in Figure 61.[1] *A* is the arrangement in the first small installations. The whole current of each tank has to flow through a copper bar connecting the tanks, and the bar must be large enough to carry this current.

B is a modification once used at Anaconda. Parallel conductors half the size of those in *A* were used, thus halving the contact resistance between conductor bars and electrodes.

A was then applied to two adjoining tanks, as shown at *C*. This resulted in halving the conductor bars required, and saved voltage. Then came the Walker system, in which any number of tanks are arranged side by side, like the two tanks in *C*. It was found advantageous to sacrifice accessibility, which was preserved on one side of each tank at *C*, to power and investment saving. It resulted in a great saving in conductor bars, and has been generally adopted. In the most recent tank house of the Raritan Copper Works (Figure 62) the saving amounted to between 45,000 lb. and 50,000 lb. of copper over what would have been required if the arrangement in the original tank house had been employed.[2] The Walker system has been still further improved by having the cathodes of one tank make direct contact with the anode of the adjacent tank by having the end of the bar supporting the cathode rest directly on the supporting hook of the anode, in place of the two resting on a common conductor placed on the side dividing the two tanks. This eliminates one contact. This contact between the cathode and the anode of the adjoining tank consists in a wedge on the top of the anode lug of 60° and a slot of 53° in the bottom of the cathode rod, thus making the wedge bind.[3] It has been found that oiling the contacts prevents corrosion and does not materially increase the resistance of the joint.

The **anodes** are cast in the desired form either directly from the converter or better from a reverberating furnace where the oxygen and sulfur dioxide contents have been reduced by poling. The standard form of casting is shown in Figure 63 as well as the method of constructing and supporting the tanks.[4] The anodes are usually

. [1] Addicks, *Copper Refining*, p. 40 (1922) ; Met. Chem. Eng. **15**, 567 (1916).
[2] Easterbrooks, Met. Chem. Eng. **6**, 247 (1908). For original tank house see Min. Ind. **9**, 269 (1901).
[3] Addicks, Min. Ind. **22**, 242 (1913).
[4] Electroch. Met. Ind. **6**, 247 (1908).
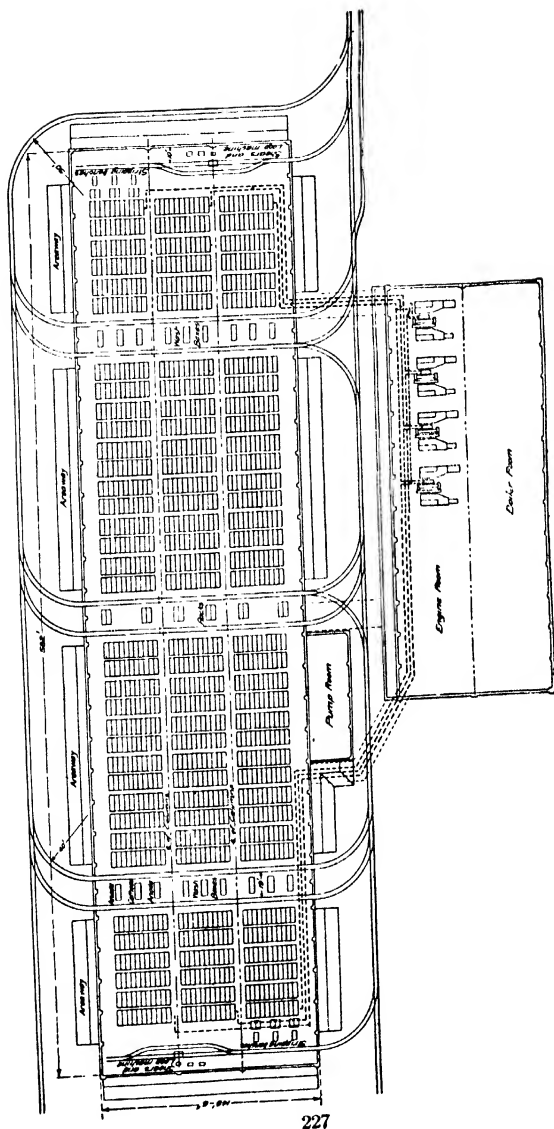
FIG. 62. — PLAN OF TANK HOUSE AT THE RARITAN COPPER WORKS

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about 3 feet square, and the whole number contained in a tank is about 30.   They are spaced 4 to $4\frac{1}{2}$ inches between centers, so that surfaces of anodes and cathodes are about $1\frac{1}{4}$ inch apart.   With an average current density of 2.16 amp./sq. dm. (20 amp./sq. ft.)

FIG. 63. — COPPER–REFINING TANKS

the current in the circuit is 10,800 amperes.   They remain in the tanks about 28 days, when all but 13 percent has been dissolved. The undissolved part is removed, washed free from slime, and remelted and cast into fresh anodes.

The **cathodes** are thin sheets of electrolytic copper called *starting sheets*, made by depositing copper on a copper " blank " whose

surface has been painted with a thin layer of grease and graphite
so that the deposited copper can be stripped off when about 1 mm.
(0.04 in.) thick.   There is one more cathode than there are anodes
in a tank.   They tend to warp after two days' electrolysis and must
be removed and straightened with wooden beaters.   The cathodes
remain in the tank from 7 to 14 days, and weigh from 180 to
230 lb. when drawn.

Figure 64 shows the method of handling electrodes in the mul-
tiple system.   After washing free from electrolyte, the cathodes
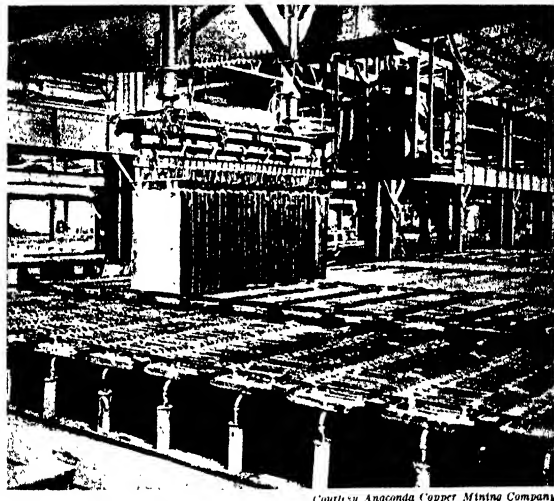
Courtesy Anaconda Copper Mining Company

FIG. 64. — LIFTING CATHODES OUT OF TANKS, RARITAN COPPER WORKS

have to be melted.   During melting copper absorbs gases and has
to be refined, first oxidizing by blowing in air and then poling to
reduce the content of oxide.   When the cuprous oxide content is
reduced to between 0.3 and 0.6 percent, the copper has reached
the " tough-pitch " stage and is ready for casting.   The shapes in
which copper is cast are shown in Figure 65.[1]   Ingots are about
10 in. long and weigh from 16 to 22 lb.   They are for remelting
for copper castings or for manufacturing alloys.   Ingot bars are
often used in place of ingots as they are more easily handled in

[1] *Copper*, Anaconda Copper Mining Company (1920).

large quantities. The notches are for the purpose of breaking up easily. Ingot bars are about 32 in. long and weigh 70 to 80 lb. Wire bars are the most popular form of refined copper bars and are used for drawing copper wire. They vary from 38 to 100 in. in length and weigh from 135 to 770 lb. The usual size is 54 in. long, weighing 200 lb. Slabs and square cakes are used for rolling, round cakes are used for manufacturing large seamless products,
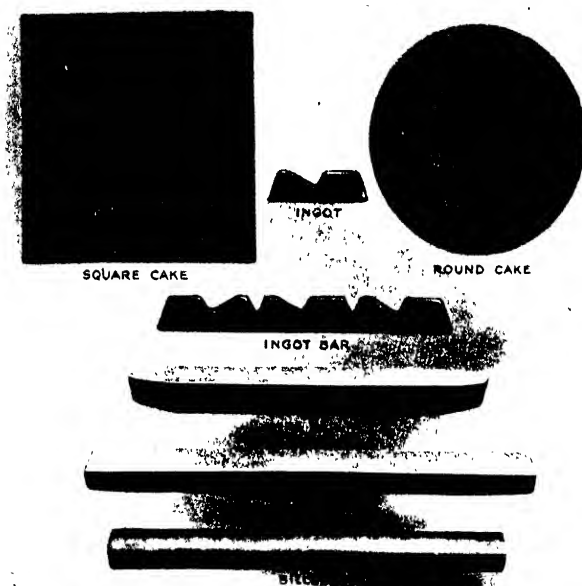
Courtesy Anaconda Copper Mining Company

FIG. 65. — SHAPES OF REFINED COPPER

such as hot-water heaters, and billets are used for making seamless copper tubing.

The **current density** [1] is of fundamental importance for the design and operation of a copper-refining plant, as upon it depend the cost of the purified copper, first cost of the plant, and the purity of the copper.

[1] Addicks, Met. Chem. Eng. **16**, 311 (1917).

At a given temperature, the current density is limited by the rate of circulation. If the current density is too high, it produces stratification of the electrolyte with its consequent irregular deposition on the cathode. The rate of circulation is limited to a degree that does not stir up the slime excessively. However, at a given rate of circulation, the higher the temperature, the greater the current density can be made, and consequently the lower the initial cost of the plant. The electric power required per kilogram of copper, assuming the temperature is kept constant, would be about 115-watt hours at a current density of 0.54 amp./sq. dm. (5 amp./sq. ft., 52 watt-hours per pound), to 840 watt-hours at 4.3
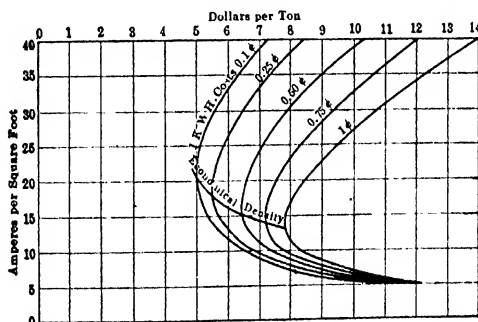
FIG. 66. — CURRENT DENSITY AND COST OF REFINING COPPER

amperes per square decimeter (40 amp./sq. ft., 381 watt-hours per pound).

A high current density always causes more impurities to be deposited on the cathode, which means a greater loss in silver and gold. About 2.16 amp./sq. dm. (from 15 to 20 amp./sq. ft.) is the current density used in most eastern refineries.

The way the cost of refined copper changes with the current density for a hypothetical case is illustrated in Figure 66.[1]

Less than the theoretical amount of copper is obtained at the cathode because of (1) current leakage, (2) because the current may produce other reactions than the deposition of copper, and (3) copper may be redissolved after deposition. If the tanks are carefully attended, the **current efficiency**[2] may be increased to 99

[1] Addicks, Met. Chem. Eng. 16, 315 (1917).
[2] Addicks, Met. Chem. Eng. 16, 23 (1917).

percent, but this is too expensive in labor. It is not economical to exceed an efficiency of 92 percent.

The current leakage may be to ground, through the electrolyte, or between the electrodes. The leakage to ground may be determined as shown in Figure 67.
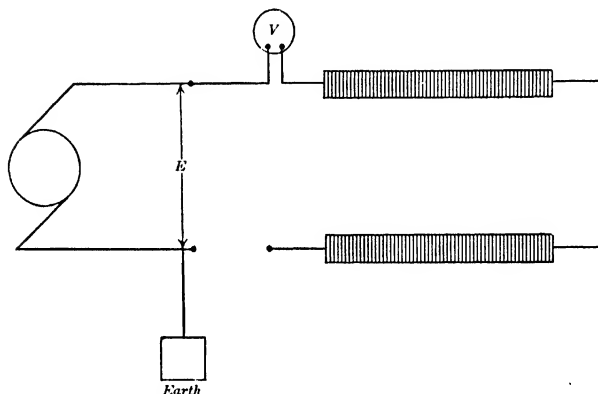
FIG. 67. — METHOD OF MEASURING CURRENT LEAKAGE TO GROUND

By means of a high-resistance voltmeter read the open-circuit voltage of the machine and then the voltage with the voltmeter as shown:

R_v = resistance of voltmeter,
R_x = resistance to earth from cells,
V = reading of voltmeter in position shown,
$\mathbf{E}$ = open circuit electromotive force of the dynamo,
I = current in voltmeter in position shown.

Then

$$\mathbf{E} = IR_v + IR_x$$

$$I = \frac{V}{R_v}. \quad \therefore \mathbf{E} = V + V\frac{R_x}{R_v}.$$

$$\therefore R_x = (\mathbf{E} - V)\frac{R_v}{V}.$$

A usual value for R_x is 5 ohms. If E is 150 volts, the current lost is 30 amperes, a small quantity compared with the main current, which would be about 10,000 amperes.

The leakage through the electrolyte consists in the flow of current from the anodes through the electrolyte to some other point than the cathodes, as to the lead lining or into the lead pipes through which the solution circulates. The copper trees in the pipes show any abnormal leakage at this point, and require removal to prevent stopping up the pipes. The leakage through the electrolyte may be determined by reading calibrated ammeters at various parts of the circuit. The readings should be identical, but for leakage to ground and through the electrolyte. It is generally found that the tanks at the far end of a circuit receive 3 to 4 percent less current than shown at the switch-board. In using instruments near conductors carrying large currents, they must be carefully protected from the magnetic field surrounding the conductor.

The lead lining of tanks becomes covered with a coating of lead sulfate which stops the leakage through the electrolyte to a large extent. This is shown by the fact that a new installation frequently has a low efficiency, though a far greater part of the initial low efficiency is due to the inexperienced inspection gang whose work is to keep the starting sheets and anodes properly separated and as nearly parallel as possible.

Current leakage may also be due to short circuits between electrodes, caused by improper spacing, by curling of starting sheets, by touching the lead lining, by omissions of electrode insulators, by treeing of the cathode deposit, by the accumulation of slimes, or by tools lying on the top of the electrodes. Treeing is prevented by the use of addition agents, by the choice of a suitable cathode age for the current density, and by circulation.

The reactions other than the deposition of copper which the current may produce are the deposition of impurities, including hydrogen, and the cyclic oxidation and reduction of the salt of any metal existing in two states of oxidation, such as iron. None of these are of any importance in the case of copper.

The loss of copper by redissolving is appreciable, amounting to about 2 percent of the deposited copper. As half of this would come from the anode, this causes a loss of 1 percent in cathode current efficiency. The chemical dissolving of the anode is affected both by its composition and by its treatment in the anode furnace. A relatively impure anode containing only 98 percent copper may have as low as 0.5 percent chemical dissolving factor.

The loss by nodules falling into the slimes is only a small fraction of a percent.

The **resistance** of a copper-refining tank consists in that of the electrolyte, the metallic conductors, contact, and back electromotive force.

On a tank for which the current density was 1.2 amp./sq. dm. (11 amp./sq. ft.) with the tank voltage 0.230 volts, the following distribution of drop was found: [1]

Between anode and anode bus-bar .... 0.0330 volt
Between cathode and cathode bus-bar .... 0.0180 volt
Across electrolyte, including drop across slimes on anode ...... 0.1790 volt

This means 78 percent of the voltage is used to force the current through the solution. The following table gives the results of resistance measurements on a different tank.[2]

	Ohms per Tank $\times 10^5$	Percent of Total
Electrolyte	4.44	55.1
Metallic conductors	1.31	16.2
Contacts	1.13	14.0
Counter electromotive force . . .	0.40	5.0
Slimes, etc., by difference	0.78	9.7

The Series System.[3] In the series system, which is used at only two refineries in this country, the American Smelting and Refining Company and the Nichols Copper Company, only the end electrodes are connected to the dynamo, those in between acting as intermediate electrodes. Copper is deposited on one face and dissolved from the other. In order to separate the refined copper from the undissolved impure copper, the surface of each electrode which faces opposite to the direction of the current is painted over with some conducting material, such as tar or a solution of resin in alcohol. The current deposits pure copper on this face and dissolves the impure copper from the other side. At the Baltimore plant the electrodes are made of rolled copper, and are of the dimensions 28 × 62 × 0.8 cm. (11 × 24¼ × $\frac{5}{16}$ in.). Two electrodes are placed in a slotted wooden frame with the adjacent edges horizontal. A single piece of copper of the area of two such electrodes would be too difficult to roll. Figure 68 will make the arrangement clear.

[1] Magnus, Electrochem. Ind. **1**, 562 (1903).
[2] Addicks, Met. Chem. Eng. **15**, 567 (1916).
[3] Haber, Z. f. Elek. **9**, 384 (1903), Electroch. Ind. **1**, 381 (1903); Hofman, *Metallurgy of Copper*, p. 534 (1914).

The slots do not reach to the bottom of the frame but a space of 7.5 cm. (3 in.) is left for the circulation of the electrolyte. The frames are of such thickness that the surfaces of adjacent electrodes are 2.2 cm. ($\frac{7}{8}$ in.) apart. The tanks cannot be lined with lead because a conducting lining would short-circuit the tank.

The Baltimore tanks are molded from asbestos, asphalt, and sand, and have the dimensions 3.6 m. long by 0.63 m. wide by 0.66 m. deep (11 ft. 10 in. by 25 in. by 26 in.). Each tank holds 135 electrodes. The tanks are arranged in parallel groups of 66, through which a current of 5000 amperes is passed, making 76 amperes
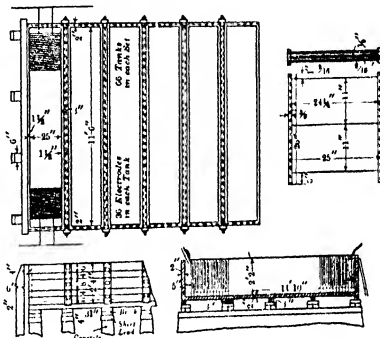
Fig. 68. — Series System, Baltimore Copper Smelting and Rolling Company

per tank. The current density is 2.26 amp./sq. dm. (21 amp./sq. ft.). About 220 volts are applied to each tank, which makes the drop between electrodes 0.16 volt. The current efficiency is 65 to 67 percent. The loss is largely due to leakage of the current through the electrolyte below the electrodes.

The corrosion of an electrode takes 17 days, when it is all dissolved except a rim on the edge where it is protected by the frame and a small patch which sometimes remains in the center. The undissolved rims are easily stripped off.

The electrolyte has about the same composition as in the multiple system. It circulates at the rate of 9.4 liters a minute (2.5 gallons) and is siphoned from the bottom of the vat at discharge. The temperature is 40° to 43° C. It would be desirable to use a higher temperature, but the material of which the tanks are made would soften.

After the impure copper has dissolved, the tank is disconnected and the electrolyte siphoned off. The electrodes are washed with a hose and the undissolved strips of impure copper are removed, and the copper is melted in a reverberatory furnace. The anode mud and the foul electrolyte are treated the same way in both systems.

The Nichols Copper Company's tanks are much larger than those of the American Smelting and Refining Company and the anodes are not held in wooden frames. The tanks, made of wood with a lining of asphalt or pitch, are 16 ft. long, 5 ft. deep, and 5.5 ft. wide. The anodes are 0.25 to 0.38 in. thick, $4\frac{1}{2}$ ft. long, 10 in. wide, and weigh 65 lb. each. Six anodes are hung in a row across a tank, with 100 rows in a tank.[1]

Comparison of the Multiple and Series Systems. The advantages claimed for the multiple system are: (1) treatment of relatively impure anode copper. Metal with more than one percent of arsenic, antimony, and bismuth, and with 200 ounces of silver per ton can be refined without collecting a prohibitive amount of silver in the cathodes, while the series system will not handle over 70 to 80 ounces of silver per ton without excessive loss in the cathodes. This is due to the tendency of the slime to settle on the cathode copper, the distance between the electrodes being small, and to the fact that some of the anode is left attached to the cathode in a form that cannot be stripped off.[2] The loss of precious metals in the cathode in the multiple system is one half that in the series system. (2) Mechanical handling of electrodes. In the multiple system a whole set of anodes or cathodes belonging to a tank are handled by an electrically driven crane, while in the series system, the manipulation of electrodes is by hand. (3) Better circulation, due to greater distance between electrodes allowing a more impure electrolyte to be used. (4) In the multiple system the slimes can be cleaned from the tanks when the first crop of cathodes is pulled, which means that 35 percent of the precious metal slime is started through the subsequent part of the process from 12 to 13 days from the time it is charged into the refining tanks.

The advantages claimed for the series system are: (1) Small power required per unit of deposited copper. The voltage between electrodes is about half that in the case of the multiple system, but the current efficiency is only about 70 percent as against 90 percent in the multiple system, so that the power required for the deposition of a given amount of copper in the series system is only 64 percent of that required in the multiple system. This is offset, however, by the increased cost of rolling the copper electrodes

[1] Ulke, *Modern Electrolytic Copper Refining*, p. 99 (1903).
[2] Min. Ind. **17**, 327 (1908); Electrochem Met. Ind. **6**, 223 (1908).

which is done at the Baltimore works, the rolling mill taking about one third the power of the plant. At the Nichols plant the electrodes are hammered straight by hand. (2) The small amount of copper tied up in the plant, due to the small number of bus-bars required, and the more frequent cleaning up and the smaller volume of solution. Due to these causes the interest on the metals locked up is one half of that in the multiple system. (3) The smaller amount of scrap produced. At Baltimore in the series system this is 3 to 6 percent of the weight of the electrode; in the multiple system, 10 to 13 percent. But at the Nichols works the scrap is said to amount to 25 percent to 30 percent,[1] probably because the anodes are not all cast to a uniform weight and thickness. (4) Formerly the amount of space required was only one quarter of that required in the multiple plant of the same output. This effected a great saving in the building as well as in the heat lost by evaporation from the tanks. This no longer applies, however, on account of the increased size of the electrodes in the multiple system. The space required in the multiple system has been thus reduced to 330 square feet per ton of copper produced per day, which is less than that required for the series system.

These different advantages counterbalance each other to such an extent that the cost of refining is practically the same in both systems, while the multiple system has the advantage of being able to treat all classes of copper bullion, and requires less care in tank-room operation.

The cost of refining copper depends on the cost of power and on the current density used. If the most economical current density is used, the total operating cost is between $5 and $8 a ton, depending on the cost of power.[2] If steam power is used, one ton of coal is required per ton of copper.[3]

Electrolytic Silver Refining. — The silver containing small amounts of gold, known as doré bullion, which is the product from smelting the slimes produced in copper refining, can be " parted " either by boiling with strong sulfuric acid, which dissolves silver and leaves gold behind, or by the electrolytic method. The sulfuric acid method is more economical for small plants, while the electrolytic is better for large plants.[4] The two principal

[1] Ulke, *Modern Electrolytic Copper Refining*, p. 100 (1903).
[2] Addicks, *Copper Refining*, p. 69 (1921).
[3] Hofman, *Metallurgy of Copper*, p. 525 (1914).
[4] Addicks, *Copper Refining*, p 192 (1921).

electrolytic methods of refining doré bullion are the Moebius and the Balbach-Thum processes.[1]

The Moebius cell, shown in Figures 69 and 70, was first used in Kansas in 1884. It is usually of acid-proof earthenware, 61 by 66 by 56 cm. deep. Each cell has four sets of four anodes 35.5 by 14 by 1 cm. thick, and five rolled cathode sheets 0.8 mm. thick, having a total cathode surface of 168 square decimeters. The anodes are contained in canvas bags to catch the anode mud and prevent its mixing with the deposited silver. Between each set of anodes and cathodes are two wooden stirrers which move back and forth, stirring the electrolyte and knocking off the loose crystals from the cathodes.

Fig. 69. — Moebius Silver-Refining Cell, Showing Anodes

The crystals collect on a tray in the bottom of the cell and are removed once or twice a day. The gold slime is removed from the bags every two or three days and is washed and treated with 1.84 specific gravity sulfuric acid in iron boiling kettles to remove silver and copper. The gold slime is then washed, dried, and cast into anodes for refining by the Wohlwill process.

The electrolyte is a neutral or very slightly acid nitrate solution contain-
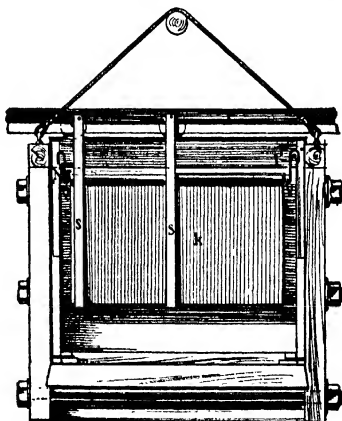
Fig. 70. — Moebius Silver-Refining Cell, Showing Cathode and Scraper

[1] Kern, Met. Chem. Eng. **9**, 443 (1911); Griswold, Tr. Am. Electroch. Soc. **35**, 251 (1919).

ing 15 to 20 grams of silver per liter and 30 to 40 grams of copper. Its resistance is 8.4 ohms per centimeter cube. The polarization is 0.15 volt.[1] A concentration of 20 to 30 grams of silver per liter is better than the more dilute solution given above. Enough electrolyte is withdrawn daily to keep the solution up to the desired purity. Waste electrolyte is treated with

FIG. 71. — MOEBIUS SILVER-REFINING CELL WITH MOVING CATHODE

copper on which silver precipitates and copper is cemented on iron after which the solution is thrown away.

A later form of Moebius cell with a traveling belt, as shown in Figure 71, is now in use at Monterey, Mexico. The tanks are 14 ft. 3 in. long, 16 in. wide, and 7 in. deep. An endless sheet of silver, C, $\frac{1}{32}$ in. thick, moves under the anodes G and carries the silver to one end of the tank, where it is carried out by the belt D and is scraped off by S. Electrical contact is made by F. The anodes are separated from the cathodes by a filter cloth as in the older process.

Side.

Plan.

End.

FIG. 72. — BALBACH-THUM SILVER-REFINING CELL

The Balbach-Thum cell, shown in Figure 72, is a shallow tank 122 by 66 by 25 cm. deep made of chemical-proof earthenware. The cathode consists of strips of Acheson graphite 2 centimeters thick, covering the bottom of the cell completely and has an area of 74 square decimeters. The National Carbon Company's hard carbon is said to be better than graphite for this purpose.

The anodes of doré bullion, 20 by 30 centimeters in area, are placed horizontally in a wooden or earthenware tray with a muslin bottom,

[1] Easterbrooks, Tr. Am. Electroch. Soc. 8, 132 (1905).

61 centimeters wide by 61 to 92 centimeters long, 10 centimeters from the cathode. Electrical contact is made with the anodes by a silver plate with a vertical lug. Silver is deposited in loose crystals on the graphite and is removed with an aluminum hoe. The electrolyte and the method of treating the slime is the same as with the Moebius cell.

The following is a comparison of the two cells.

	CURRENT DENSITY, AMP /SQ DM.	VOLTAGE	CURRENT EFFI- CIENCY IN PERCENT	PERCENT DAILY OUTPUT OF SILVER TIED UP	ANODE SCRAP	YIELD, KILO- GRAMS PER KILO- WATT DAY
Moebius, earlier form .	2.2 to 5.4	1.4 to 1.7	92 to 95	10 to 50	Small amount	54
Balbach-Thum	Cathode 2.2; anode, 4.3	3.2 to 3.8	93 to 95	32	None	22–24

The advantages of Moebius cells over the Balbach-Thum cells are: (1) less energy required per unit of product, (2) require one sixth the space for a given daily capacity, (3) less nitric acid consumed by reduction to ammonia. The advantages of Balbach-Thum cells over Moebius cells are: (1) less care necessary to prevent gold loss, (2) always open to inspection, (3) no anode scrap, (4) less repair cost, and (5) less time lost in removing silver and sludge, (6) less labor. The cost of refining by the Moebius process is 8 to 16 cents per kilogram.

A third method, called the Whitehead process, used in some of the government plants, uses gelatin to make the silver come down in a coherent form. It is stripped from silver cathodes.[1]

As compared with the sulfuric acid method, the electrolytic gives a purer product, the danger of metal loss is less, in a large plant the operating costs are lower, and little by-product liquors are made. The first cost, however, is greater and the metal tie-up is 50 percent more.[2]

The separation of silver and copper in alloys consisting of approximately equal parts of silver and copper, such as silversmiths' waste, requires a different procedure, such as the Dietzel process,[3]

[1] Addicks, *Copper Refining*, p. 116 (1921).
[2] Addicks, *Copper Refining*, pp. 114 and 192 (1921), and Kern, *l.c.*
[3] Z. f. Elektroch. **6**, 81 (1899–1900).

used at the Gold- und Silber-Scheide Anstalt at Pforzheim.   This
depends on dissolving both copper and silver in a weakly acid
solution of copper nitrate at the anode and carrying this solution
immediately into another vessel where the silver is precipitated by
contact with copper.   After the silver has been thus completely
removed, the copper nitrate solution is made slightly acid and
enters the electrolyzing vat, where a certain amount of the copper
is deposited as it passes the cathode.   The arrangement is shown
in Figure 73, which repre-
sents a cross section of the
dissolving vessel. KK are
the rotary cylindrical copper
cathodes, coated with a thin
layer of grease or graphite, on
which the deposition of cop-
per takes place.   When the
copper grows out in the form
of trees, it is knocked off.
The copper cylinders are
suspended on flanged contact
rollers, which, when set in
motion, cause the cylinders
to rotate.   Thus the shafts
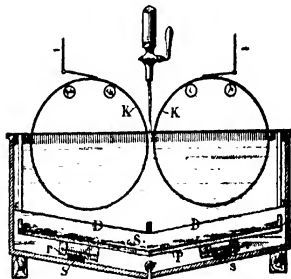
FIG. 73. -- DIETZEL SILVER-REFINING CELL

and driving mechanism are out of contact with the solution. P is
a loose bottom for supporting the material to be treated, S, and is
of hard rubber, celluloid, or glass.   The plates P are provided
with platinum wires for conducting the current to S. DD are filter
cloths, the object of which is to catch any copper falling from the
cathodes and to prevent any of the anodic silver solution from
rising to the cathode.   The desilverized electrolyte is admitted
from above, as shown.   A small amount of silver — 0.03 percent
— is deposited at the cathode with the copper.   The solution con-
tains from 2 to 5 percent of copper and 0.05 to 0.4 percent of free
nitric acid.   The current density is 1.5 amperes per square decime-
ter (14 amperes per square foot) and the voltage is from $2\frac{1}{2}$ to 3
volts.

Electrolytic Gold Refining. — The electrolytic refining of gold
was first accomplished by Wohlwill [1] at the Norddeutsche Affinerie

[1] Z. f. Elektroch. **4**, 379, 402, 421 (1898); U. S. Pat. 625,863; 625,864;
Tuttle, Electroch. Ind **1**, 157 (1903); Wohlwill, Electroch. Ind. **2**, 221, and
261 (1904); Whitehead, Electrochem. Met. Ind **6**, 355 and 408 (1908); Kern,
Chem. Met. Eng. **9**, 143 (1911).

in Hamburg. The process consists in electrolyzing gold anodes in a hot acid solution of gold chloride. A cyanide solution would not do, because silver and copper would be deposited with the gold. Wohlwill found that gold anodes do not dissolve when electrolyzed in a solution of gold chloride, $AuCl_3$, or of chloroauric acid, $HAuCl_4$, but that in both cases chlorine is set free. In the solution of chloroauric acid the chlorine may be mixed with oxygen when the current density is low or the solution dilute. In order to have the gold dissolve, there must be some free chloride present, either hydrochloric acid, which is commonly used, or some alkali chloride. At a definite temperature there is a definite amount of free acid for every current density that will prevent the evolution of chlorine. The amount of free acid required decreases with increasing temperature. With a solution containing 3 percent of hydrochloric acid and 30 grams of gold per liter, at 70° C., for anodes containing less than 6 percent silver and lead (940 fine) the current density can be 15 amp./sq. dm. and more; with 10 percent silver 9 amp./sq. dm. is satisfactory. In case chlorine appears at the anode, its evolution can be stopped by adding hydrochloric acid, or by raising the temperature.

The gold is formed on the cathode in large crystalline deposits which adhere in such a way that they can be easily removed mechanically. The more gold in solution, the more compact the deposit, while an increase in the current density has the opposite effect.

The anodic behavior of gold in a solution of $AuCl_3$ is shown in
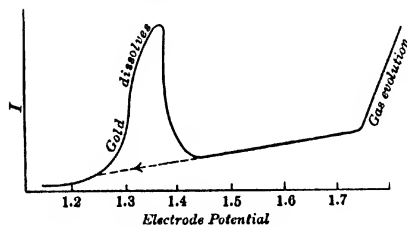
FIG. 74. — ANODIC BEHAVIOR OF GOLD IN AuCl₃ SOLUTION

Figure 74.[1] At 1.2 volts the current increases but falls rapidly after reaching 1.38 volts and at 1.73 volts gas evolution begins, and there is no solution of gold. In the presence of hydrochloric acid, there is no fundamental difference; passivity only occurs at a higher current density. On lowering the electrode potential there is a hysteresis shown by the dotted line.

[1] Coehn and Jacobson, Z. anorg. Ch. **55**, 330 (1907).

Gold, like copper, dissolves both in the univalent and trivalent states. The electrode potential of Au/Au^{+++} is more negative than that of Au/Au^+ for equal ion concentrations, so the principal part of the gold dissolves in the trivalent state. Univalent gold does not change as rapidly to trivalent with the deposition of gold as the corresponding reaction for copper, so that considerable univalent gold reaches the cathode, which of course increases the quantity deposited per faraday by the amount in which the univalent gold is in excess of the equilibrium concentration.

The higher the current density at the anode, the more positive the electrode potential, and the more gold should go into solution as univalent ions. This apparently does not agree with the result of Wohlwill, shown below, that the higher the current density the closer the agreement between the anode loss and the cathode gain.[1]

Current Density Amp./Sq Dm	Cathode Gain for One Ampere-Hour	Anode Loss for One Ampere-Hour
15.	2.48	2.57
7.4	2.53	2.80
6.0	2.8	3.2

Foerster's explanation is that these results show only that at high current density less univalent gold gets away from the anode. Since the further an unstable state is removed from equilibrium the more rapidly equilibrium is reached, it follows that the more univalent ions are produced the more completely the reaction $3\,Au^+ = Au^{+++} + 2\,Au$ takes place at the anode. The gold thus separated settles in the anode and is again subject to electrolytic solution.

The tanks used in gold refining are of porcelain; at the Philadelphia mint they are 38 cm. by 28 cm. by 21 cm. deep; at the San Francisco mint, 46 cm. by 33 cm. by 30 cm. deep.

If there is lead in the anodes, the electrolyte contains 1 to 2 percent sulfuric acid in addition to the gold chloride and free hydrochloric acid, to precipitate the lead. Gold chloride solution has to be added every day to make up for the excess of gold deposited over that dissolved at the anode. The tanks are heated by placing on sand beds heated by steam pipes. Circulation is either by gravity through about 12 tanks in cascade, or by a

[1] Z. Elektroch. 4, 408 (1898). The results are calculated from Wohlwill's data in Foerster's *Elektrochemie wasseriger Lösungen*, p. 533 (1921).

propeller in each tank. The cascade system gives more uniform circulation.

The cathodes are fine sheet gold about 0.3 mm. thick. The anodes have to be of such a thickness that they are used up in 24 hours, in order to cut down the interest on the gold tied up. Anodes 940 fine (94 percent pure) are 15 cm. long, 7.5 cm. wide by 1 cm. thick. The anodes and cathodes are placed with their centers 1.9 cm. apart.

With a current density of 8.5 to 13 amp./sq. dm. the voltage per tank is 1 to 1.3 volts. The yield is about 80 kilograms per kilowatt-day of gold 999.8 fine.

Anodes are usually between 880 and 960 fine. The anode mud may consist of gold, silver chloride, lead sulfate, iridium, and osmium. Silver is recovered by fusion with sodium carbonate according to the reaction:

$$2\ AgCl + Na_2CO_3 = 2\ Ag + 2\ NaCl + CO_2 + O.$$
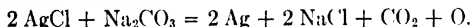
Iridium and osmium are separated from silver by acid parting. Copper, platinum, and palladium go in solution at the anode. Palladium does not deposit at the cathode unless its concentration is more than 5 percent. Platinum and palladium are precipitated with ammonium chloride, ignited to change to the metallic state, and palladium is dissolved with nitric acid.

Pulsating Current. — If silver in the anode exceeds six percent, it has to be removed mechanically, but Wohlwill found that if a pulsating current is used, the current density can be increased considerably without the necessity of cleaning off silver chloride.[1]

There is some benefit even if the maximum value of the alternating voltage is less than the value of the direct, but it is better to have the alternating voltage so large that there is a reversal of the current. The alternating- and the direct-current generators are connected in series and designed so as to carry the current resulting from both. The larger the ratio of the alternating to the direct voltage the greater the quantity of impurity allowable in the anode. In the old method, with 10 percent silver in the gold, 7.5 amp./sq. dm. is the limiting workable current density and silver chloride has to be scraped from the anodes every 45 minutes. With the alternating current 1.1 times the direct, 12.5 amp./sq. dm. can be used without scraping, while if this ratio is 1.7, anodes with 20 percent silver can be refined with 12 amp./sq. dm. Other advantages of the pulsating current are: (1) it prevents the libera-

[1] Z. Elektroch. **16**, 25 (1910); Met. Chem. Eng. **8**, 82 (1910).

tion of chlorine; (2) it allows higher current densities; (3) there is less gold in the anode mud; and (4) a low temperature, 25° to 35° C., can be used, giving dense deposits. A direct-current voltmeter shows a lower reading across a cell with a pulsating current than with an equivalent direct current. The amount of gold dissolved and deposited is, of course, not affected by the alternating current.

Electrolytic Iron Refining. — Until within the last ten years electrolytic iron was used technically only for facing dies and electrotypes. Recently a number of processes have been put into operation for refining iron.

Iron is more electronegative than hydrogen, and there is considerable resistance to its deposition, that is, the value of η_M is high. It can therefore be deposited only from solutions which have low hydrogen-ion concentrations.

In 1868 Varrentrapp [1] produced deposits 2 mm. thick by electrolyzing a solution of ferrous sulfate and ammonium chloride for 14 days, and many since have succeeded in depositing thick layers of iron.[2]

Burgess and Hambuechen [3] refined iron for many months using a solution containing 40 g. of iron per liter as iron sulfate and 40 g. of ammonium chloride, at a cathode current density of 0.66 to 1.1 amp./sq. dm. and a potential difference of 1 volt. The temperature was 30° C. The current efficiency was nearly 100 percent and the purity of the deposit 99.97 percent.

One of the best solutions is that of F. Fischer,[4] consisting of 450 g. ferrous chloride, 500 g. calcium chloride, and 750 g. water, electrolyzed at 90° to 110° C. This has been put into operation by the Langbein-Pfanhauser works in Leipzig.[5]

The Société Le Fer electrolytic process for making boiler tubes has been in operation for the past six years at Grenoble in successful competition with other methods.[6] The electrolyte is ferrous chloride. The anodes are cast scrap iron, and the cathodes are rotating cylinders. The cathode current density is

[1] Ding. Polytech. J. **187**, 152 (1868); Hughes, Tr. Am. Electroch. Soc. **40**, 201 (1921).

[2] For account of these, see Hughes, *l.c.*

[3] Tr. Am. Electroch. Soc. **5**, 201 (1904); **19**, 181 (1911).

[4] Hughes, *l.c.*, p. **200**; Germ. Pat. 212,994 (1908);   228,893 (1909); 230,876 (1910).

[5] Z. Elektroch. **15**, 595 (1909).

[6] Escard, Le Genie Civil, **75**, 165, 199, and 225 (1919); Stoughton, Tr. Am. Electroch. Soc. **40**, 225 (1921).

10 amp./sq. dm. Hydrogen bubbles are said to be prevented as far as possible by the addition of depolarizers to the electrolyte. The occluded hydrogen is driven off by annealing in an oil bath at 300° C., after which the tubes are as malleable as pure copper.

The finished tubes have the following analysis:

	PERCENT
Iron	99.967
Carbon	0.008
Manganese	0.009
Silicon	0.014
Sulfur	Traces
Phosphorus	0.002

Since 1916 the Western Electric Company has had a plant in operation at Hawthorne, Illinois, refining 25,000 pounds of iron a week.[1]

The solution is ferrous sulfate, ferrous chloride, and ammonium chloride.

The anodes are mild steel; the cathodes, polished steel, from which the deposit is stripped when 0.3 to 0.6 cm. thick. ($\frac{1}{8}$ to $\frac{1}{4}$ in.). The current density is 1.3 amp./sq. ft. The cathode iron is very brittle and is ground to powder, the particles are insulated, and the powder is then pressed into solid rings, which are used as cores of the induction coils in electrical transmission circuits. Several hundred tons of electrolytic iron are used annually for this purpose.

The following data, with design of an iron-refining plant, are given by McMahon:[2] wooden tanks, without a lining, 10 ft. long, 3 ft. wide, 4 ft. deep; circulation, 3 gal./min. with continual filtering. The iron is stripped, when $\frac{1}{4}$ in. thick, from cold-rolled steel cathodes, which are $3\frac{2}{3}$ ft. long, $2\frac{1}{2}$ ft. wide, and $\frac{3}{16}$ in. thick, riveted to copper bars. They are stripped every 12 to 13 days. Each

IMPURITY	PERCENT IN ANODES	PERCENT IN CATHODES	PERCENT REMOVED, OR REFINING EFFICIENCY
Carbon	0.60	0.014	97.7
Phosphorus	0.05	0.013	74.0
Silicon	0.23	0.028	87.8
Manganese	0.30 to 0.50	0.029	90 to 94
Sulfur	0.10	0.003	97

[1] Speed and Elmen, J. Am. Inst. E. E. **40**, 596 (1921); Elmen, Tr. Am. Electroch. Soc. **40**, 228 (1921).

[2] Chem. Met. Eng. **26**, 639 (1922).

tank has 16 anodes and 15 cathodes. The solution contains 60 g. of iron, 25 g. of chlorine, and 25 g. of ammonia per liter with a small amount of glue, and is electrolyzed at 45° C. The anodes are 2 in. thick and should be as pure as possible. The usual analysis of anodes and corresponding cathodes is as given in the table on the preceding page.

The yield is about 1.5 lb./kw.-hr. or 16.3 kg./kw.-day.

Electrolytic Zinc Refining. — It was shown above that in extracting zinc, the solution has to be carefully purified in order to get a satisfactory zinc deposit. In zinc refining therefore the impurities in the anode must either not be allowed to go into the solution to any appreciable extent, or the solution must be purified frequently. Preventing solution is accomplished by using a solution in which some of the impurities are insoluble, and in keeping others which would dissolve, but which are more electropositive than zinc, in contact with the zinc anodes so that they will precipitate as rapidly as they dissolve.

Impure zinc occurs in three forms, all of which can be refined electrolytically. These are: (1) galvanizers' hard dross, (2) zinc crust in the Parkes process from desilverizing lead, and (3) ordinary spelter.

(1) Zinc for hot galvanizing is held in iron pots, and gradually becomes contaminated with iron. When the iron dissolved amounts to about 6 percent, the zinc is removed and cast into ingots. This galvanizers' dross also contains 1 to 3 percent of lead, and sometimes as much as 2 percent of tin. Its market price is about 70 percent of that of commercial zinc, which leaves about 20 percent of the price of commercial zinc as a margin for refining and profit. This margin would be about $18 to $25 a ton, so that to offer any inducements of profit the cost of refining should not be over $15 a ton.[1]

Richards experimented on the electrolytic refining of the residue obtained from this dross by allowing to stand for some time just above the melting point and skimming off 25 percent of its weight as salable zinc. One tenth of one percent of aluminum was added to prevent liquation and swelling in the molds on casting anodes from this skimmed product. The anodes, 2.5 to 4 cm. thick and 45 cm. wide by 120 cm. long, were hung 4 cm. from the cathode plates, which consisted of rolled zinc 0.62 cm. thick. The cathodes were greased to prevent adhesion of the deposit and were painted on the edges with black asphaltum varnish to prevent deposition on

[1] J. W. Richards, Tr. Am. Electroch. Soc. **25**, 283 (1914).

them. The electrolyte contained 15 percent of zinc sulfate hepta-
hydrate, 1.7 percent acetic acid, and 0.8 percent sodium acetate.
The working temperature was 31° C., the voltage drop per tank
1.25 volts, and the current density 1 amp./sq. dm. Good
deposits were obtained for 3 to 4 days, and if the trees were re-
moved, they could be run six days in all, and give clean plates.
The current yield was 100 percent at first, but fell to 80 or 90
percent when the plates became spongy. The loss in weight on
melting was 20 to 25 percent of the deposit. This could be
reduced by using ammonium chloride, but this added consider-
ably to the expense. The zinc was 99.95 percent pure. The
ferrous sulfate was precipitated as ferric hydroxide by injecting
air into the tanks through rubber hose. A current of the electro-
lyte flowed out of each tank, and was filtered. The iron might
also be precipitated by zinc oxide. It was found that though
the process worked well, the margin of profit was too small to
justify the building of a plant.

(2) In 1886 Rössing [1] published a process for refining zinc from
the zinc scum of a lead refinery at Tarnowitz. At that time the
scum contained too much lead, but later when the zinc content of
the scum was increased, it was taken up again and used for a while
and then discontinued.[2]

The zinc scum had the following composition in percent:

Silver	. . . .	11.32
Lead	. . . .	3.13
Copper	. . . .	6.16
Nickel	. . . .	0.51
Iron	. . . .	0.24
Zinc	. . . .	78.64
Antimony, arsenic, bismuth, traces.		

This was cast into anodes weighing 20 to 30 kilograms. The
cathodes were starting sheets produced electrolytically on rolled
zinc plates. Greasing the plates for stripping the sheets was not
necessary. The electrolysis tanks were 75 cm. long, 60 cm. wide,
and 70 cm. deep. The electrolyte was zinc sulfate at 15° to 20° C.
The current density was 0.8 to 0.9 amp./sq. dm., at which the
anodes lasted 4 to 6 days, and the cathodes were changed every
3 to 4 days. The slime was removed every 8 to 14 days. Less
frequent removals allowed too much to dissolve. The slime con-
sisted of zinc, silver, lead, and copper. This was treated with

[1] Germ. Pat. 33, 589; Z. f. Berg.- und Hüttenm. Ztg., 1886, p. 463.
[2] Hasse, Z. f. Berg-, Hüttenm.- und Salinen-Wesen, 45, 322 (1897).

dilute sulfuric acid, leaving lead, copper, and silver for further separation.

(3) The refining of spelter was tested out by the American Smelting and Refining Company during 1914–16. It was found more profitable than the distillation method, but not as profitable as to convert to zinc oxide.[1]

Zinc or " spelter " is classified in four grades :[2]

	Percent Lead	Percent Iron	Percent Cadmium	Percent Total, Maximum
A. High-grade	0.07	0.03	0.05	0.10
B. Intermediate	0.20	0.03	0.05	0.50
C. Brass Special	0.75	0.04	0.75	1.20
D. Prime Western	1.50	0.08	——	——

These grades of zinc have no precious metals, and usually the difference in value of grade A and grade D is 1¢ to 2¢ a pound. During the war the demand for grade A for making cartridge-brass was so great that the prices of A and D were 12¢ and 18¢ a pound respectively. Also grade D zinc containing 1 percent of cadmium is easily obtainable, so that each pound of zinc contains cadmium worth 1¢ with cadmium at $1.40 a pound. Under these conditions, the Electrolytic Zinc Company near Baltimore refined grade D zinc to grade A.[3]

The anodes were 61 cm. wide by 76 cm. immersed, and 1.9 cm thick with lugs as in copper refining. They were placed in canvas bags tightly drawn by strings and wooden strips, to hold the anode mud in contact with the anodes. The cathodes were $\frac{1}{16}$-inch aluminum sheets one inch larger all around than the anodes and with wooden strips around the edges. The electrolyte contained 4 to 10 percent zinc as sulfate and 1 to 5 g./l. of free sulfuric acid. Iron up to 1 g./l. did no harm to the deposit. Zinc and iron had to be removed continually, and sulfuric acid added.

The tanks were wood lined with asphalt, 196 cm. long by 91 cm. wide and 117 cm. deep. The circulation was 11.4 liters per minute. The cathodes were stripped every four days, and the anodes lasted fourteen days. The slime was held by the bags in a layer 10 mm. deep. It contained 50 to 60 percent zinc, 2 to 5 percent

[1] Ralston, *Hydrometallurgy of Zinc*, p. 149 (1921).
[2] Am. Soc. for Testing Materials Proc. **11**, 147 (1911).
[3] Ralston, *l.c.*, p. 150; Bryan and Aldrich, U. S. Pat. 1,299,414 (1919).

iron, with cadmium and lead in varying proportions. The slime was dissolved in sulfuric or hydrochloric acid and the cadmium precipitated by zinc dust. The plant was dismantled when the large difference in price of the two grades of zinc disappeared.

Electrolytic Nickel Refining. — Nickel was refined by the Balbach Company at Newark, N. J., from 1894 to 1900. The anodes, containing 94 to 97 percent nickel, were furnished by the Oxford Copper Company. The details of the process were kept secret. The product contained 0.25 percent iron and a small amount of cobalt.[1] The process was given up probably because of the large amount of anode scrap and the expense of remelting to anodes. Also the voltage is relatively high, requiring a large amount of power, and it is doubtful whether the impurities in crude nickel are of sufficient value to make refining profitable.

Electrolytic Lead Refining. — Lead is an ideal metal to refine electrolytically, on account of its high electrochemical equivalent and of its relatively electronegative position in the electrolytic series. Its greater tendency to go into solution than that of most of the metals occurring in it as impurities makes it possible to dissolve the lead, leaving the impurities behind in the metallic state. This avoids contaminating the electrolyte, which consequently does not need frequent purification. The principal electrolytic difficulty to overcome was to obtain the lead in a coherent, compact form from a solution that would not be too expensive to use on a commercial scale. The chloride or sulfate, which are usually the salts employed for metal refining, cannot be used in the case of lead on account of their insolubility. The problem has been solved by A. G. Betts,[2] who found that a solution of lead fluosilicate with a small quantity of gelatin fulfilled the requirements. The fluosilicate solution is not the only one from which a good deposit can be obtained; but it was selected on account of its low price as compared with other solutions giving equally good deposits.[3] The object in refining lead is to recover the copper, antimony, and bismuth, as well as the gold and silver. Bismuth is said to be the mainstay of lead refining.[4]

The solution of lead fluosilicate ($PbSiF_6$) is prepared by adding white lead or lead carbonate to fluosilicic acid. Fluosilicic acid

[1] Ulke, Electrochem. Ind. **1**, 208 (1903).

[2] See *Lead Refining by Electrolysis*, by A. G. Betts. John Wiley and Sons (1908).

[3] Betts, *ibid.*, p. 17.

[4] Addicks, Met. Chem. Eng. **17**, 169 (1917).

is prepared by allowing a solution of hydrofluoric acid, made from sulfuric acid and calcium fluoride, to trickle through a layer of pure sand or broken quartz. Heat is applied to start the reaction, which then furnishes sufficient heat itself to maintain the necessary temperature. No precipitate is formed on adding the lead to the acid unless an excess of lead is added,[1] and the solution obtained is colorless. The strength of the solution ordinarily employed in practice is from 6 to 7 grams of lead, and from 12 to 13 grams of SiF_6 per 100 cubic centimeters.[2] This means about 8 grams of free fluosilicic acid per 100 cubic centimeters of solution. The gelatin is added to the solution as a hot strong solution of glue. Enough is added to make its concentration 0.1 percent, and $\frac{1}{2}$ to $\frac{3}{4}$ of a pound is required per ton of lead deposited. The temperature of the electrolyte has been found to have no effect in the character of the lead deposit.[3] In practice about 30° C. is maintained by the current itself.

The impurities in the anode may consist of iron, zinc, sulfur, copper, nickel, tin, antimony, arsenic, bismuth, cadmium, gold, selenium, and tellurium. Only the zinc, iron, nickel, and tin would go into solution, as the other metals are all more positive than lead and would therefore remain in the anode slime. Zinc, iron, and nickel are more negative than lead and would therefore not be precipitated from the solution with lead. Tin, however, is so near lead in the value of its electrode potential that it dissolves and precipitates with the same facility and can therefore not be separated from lead electrolytically. It must be removed by poling, before casting the anodes. When only 0.02 percent of tin is in the anode, it is found in the cathode.[4] With this exception, the impurities are easily prevented from reaching the cathode, even when present in the anode in large quantities. Pure lead can be obtained when the anode contains only 65 percent lead, the rest being impurities of bismuth, antimony, arsenic, silver, and copper.[5] A low current density — 4 amp./sq. ft. — was required with anodes of this composition.

The slime nearly all adheres to the anode and is consequently easily removed from the bath. Its composition of course depends on that of the anodes. The following is a sample analysis from

[1] Betts, l.c., p. 30. See also Senn, Z. f. Elektroch. 11, 230 (1905).
[2] Betts, l.c., p. 255.
[3] Senn, l.c.
[4] Betts, l.c., p. 46.
[5] Betts, l.c., p. 56.

Trail, in percent: Cu, 9.50; Ag, 17.10; Sb, 25.91; As, 5.96; Pb, 14.50; ounces of gold per ton, 34.50. The anode scrap is about 20 percent of the original anode. The method of working up slime employed at Trail, British Columbia, by the Consolidated Mining and Smelting Company of Canada, consists in treating with sodium sulfide, which extracts 80 per cent of the antimony and some arsenic. The antimony is then deposited electrolytically on steel cathodes using lead anodes at a current efficiency of about 45 percent. The sodium sulfide is changed to thiosulfate. Bismuth is also recovered by depositing electrolytically in a granular form.

The cathodes used in lead refining are thin sheets of pure lead. The current density allowable depends on the purity of the anodes. As stated above, anodes containing only 65 percent lead can be refined if the current density is as low as 4 amp./sq. ft. In practice the anodes are about 98 percent pure,[1] and the current density is from 12 to 16 amp./sq. ft. (1.3 to 1.7 amp./sq. dm.). The current efficiency is from 88 to 95 percent. The analysis of refined lead from Trail shows a purity of about 99.995 percent. The average voltage per tank is from 0.30 to 0.38 volt and the polarization amounts to 0.02 volt. The tanks, made of southern yellow pine, are arranged in the multiple system. The electrolyte is caused to circulate by having the difference in the level of two successive tanks from $2\frac{1}{2}$ to 3 inches. Five gallons per minute is a fair amount of circulation for a 4000-ampere tank.

Lead is refined electrolytically at Trail, British Columbia, Newcastle-upon-Tyne, England, by the United States Metals Refining Company at Grasselli, Indiana, and by the American Smelting and Refining Company at Omaha. The plant at Trail has been operated since 1902, with a capacity of 80 tons a day. A detailed description of the plants at Trail and Grasselli will be found in Betts's treatise, referred to above.

Electrolytic Tin Refining. — In sodium hydrate tin dissolves anodically more easily in the stannous state to form stannite, than to form stannate:

$$Sn + 2F = Sn^{++}, \tag{1}$$

$$Sn^{++} + 3 OH^- = HSnO_2^- + H_2O. \tag{2}$$
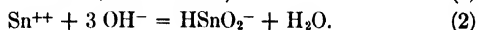
But the electrode potentials of the reactions (1) and

$$Sn^{++} + 2F = Sn^{++++}, \tag{3}$$

---
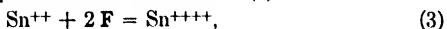
[1] For the following statements, see Betts, *l c.*, p. 287, Table 110; p. 255, Table 91; p. 287, Table 108; and p. 189, Table 73.

for equal concentrations of stannate and stannite are very nearly equal, so that the little increase in the electrode potential due to a film produced by the anode slime is sufficient to oxidize the stannous to the stannic state according to (3) with the formation of stannate:

$$Sn^{++++} + 6\, OH^- = SnO_3^{--} + 3\, H_2O. \tag{4}$$
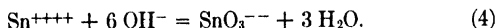
Scraping the anode causes it to become active again for a short while.[1]

In electrolyzing at the cathode a solution of stannite and stannate, stannate is not first reduced to stannite as would be expected from the relative positions of the electrode potentials:

$$Sn/Sn^{++} = -\, 0.136$$

and

$$Sn^{++}/Sn^{++++} = +\, 0.131,$$

but all stannite is decomposed with the deposition of stannous tin and then tin is deposited from the stannate without the formation of appreciable amounts of stannite.[2] This is because of the considerable chemical polarization of the reaction:[3]

$$Sn^{++++} - 2\, F = Sn^{++}. \tag{5}$$
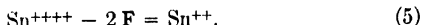
Tin therefore behaves as a quadrivalent metal in refining in an alkaline solution.

The only other possible cathode reaction is the deposition of hydrogen. This is less the higher the concentration of tin and the greater the alkalinity.

Detinning scrap tin plate and old tin cans may be considered a refining operation in which tin is removed from the underlying impurity of iron. An electrolytic process for this purpose was developed by Goldschmidt,[4] and for ten or fifteen years was the principal method of recovering tin from tin scrap. Goldschmidt abandoned the process in 1907[5] for the chlorine detinning method,

[1] Foerster and Dolch, Z. Elektroch. **16**, 599 (1910).

[2] Naef, Dissertation, in Foerster, *Elektrochemie wasseriger Lösungen*, p. 542 (1922).

[3] Foerster and Yamasaki, Z. Elektroch. **17**, 361 (1911).

[4] Mennicke, Z. Elektroch **8**, 315, 357, 381 (1902); Goldschmidt, Z. angew. Ch. **22**, 1 (1909). For an account of the different solutions proposed for this process, as well as for tin plating and refining, see Kern, Tr. Am. Electroch. Soc. **23**, 193 (1913).

[5] Met. Chem. Eng. **17**, 187 (1917).

though this process was reported in operation in three factories in Italy in 1912.[1]

Tin scrap contains from 2 to 3.5 percent tin. This is placed in iron-wire baskets, reënforced by heavy angle irons, and electrolyzed as anode in a sodium hydrate solution containing about 10 percent sodium hydrate with 2 percent tin as stannate. The temperature is 70° C. on account of the lower resistance at high temperature. The iron electrolytic tanks also act as cathodes. Each tank contains three baskets, taking up about ⅔ of the volume of the tank. In a tank containing 3 cubic meters, each basket holds 50 kg. of scrap. Extra sheet-iron cathodes are suspended between the baskets. In order to expose all the surface of the scrap to the action of the current, it has to be turned over by hand with iron forks. Under normal working conditions the time required for dissolving the tin from the anode is 5 to 7 hours, at 1.5 volts between anode and cathode. The electrolyte circulates from the electrolytic cells to heating vats, and back through the cells, which are all in the same level and not in cascade. The scrap still contains 0.1 to 0.2 percent tin after extraction.

The tin deposit is in a granular form which is easily removed from the cathode. It is washed, compressed, and melted by immersing in melted tin. The following are the analyses of the electrolytic tin before and after purification by smelting with carbon and slag-forming material:

	Percent Tin	Percent Lead	Percent Copper	Percent Iron
Electrolytic tin before purifying by smelting	95.27	2.37	0.09	2.17
Electrolytic tin after purification .	98.74	1.09	0.05	0.12

The cathode current density is about 1 amp./sq. dm. and the current efficiency is about 50 percent calculated for bivalent tin, or nearly 100 percent for quadrivalent.[2] The Italian plants are said to employ a current density of 0.75 amp./sq. dm., and to detin in 3 hours.[3]

The electrolyte absorbs carbon dioxide from the air and requires constant purification. The presence of carbonate reduces the

[1] Met. Chem. Eng. **10**, 202 (1912).
[2] Foerster, *Elektrochemie wasseriger Lösungen*, p. 545 (1922).
[3] Met. Chem Eng. **10**, 202 (1912).

conductance, the current yield is lowered, and the time required for detinning is longer.

In the Italian plants referred to above fresh solution has to be added to the electrolyte every two days; about one tenth of the whole solution has to be replaced every week.

The electrolyte is purified by saturating with carbonic acid for precipitation of stannic acid, which is sold as a by-product, while the filtrate is causticized with lime and put back into the process.

The nature of the electrolyte makes this a very difficult process to maintain in smooth working order, and there are considerable losses in tin due to the large surfaces that have to be washed free of the solution.   It is for these reasons that it was given up.

During the war the supply of tin came largely from South America, and contained impurities not easily removed by fire-refining [1] and in some cases this tin contained gold and silver.   Electrolytic tin refining was therefore started by the American Smelting and Refining Company at Maurer, New Jersey.   At first a fluosilicate solution was used,[2] with the addition of sulfuric acid for the precipitation of lead.   The composition was 4 to 5 g. tin, 4.5 to 7.5 g. of free H_2SiF_6 (10 to 13 g. total H_2SiF_6), 1 to 2.5 g. of sulfuric acid, and 0.5 to 1.5 g. of hydrofluoric acid per 100 cc.   Glue, cresol, and oil were used as addition agents.   The current density was 1.10 to 1.32 amp./sq. dm.   The composition of anodes and cathodes was as follows all in percent except gold and silver, which are in g./1000 kg.

ANODES

Sn	Pb	Cu	Bi	As	Sb	Ag	Au
94–98	0.5–1.3	0.3–0.6	0.5–3.5	0.02–0.35	0.1–0.25	0.017–0.03	0.34–0.68

CATHODES

Sn	Pb	Cu	Bi	As	Sb	Ag	Au
99.2–99.9	——	0.015–0.03	0.02–0.05	0.01–0.0015	0.01–0.09	——	——

This solution has been replaced by one containing 6 g. of tin as sulfate and 5 g. of sulfuric acid per 100 cc.

Tin is also refined in sodium sulfide solution.   The electrolysis cells are 2.5 m. long, 0.7 m. wide, and 0.9 m. deep.   The cathodes are thin cast sheets of pure tin of the same dimensions as the anodes, which are cast from crude tin 0.5 m. wide, 0.75 m. long, and 1 cm. thick.   The number of anodes per cell is 30, the cathodes 29, 3 to

[1] Kern, Tr. Am. Electroch. Soc. **33**, 156 (1918); **38**, 143 (1920).
[2] Kern, Tr. Am. Electroch. Soc. **38**, 165 (1920).

3½ cm. apart. The electrolyte contains at least 10 percent of sodium sulfide, heated by a steam coil placed in the bottom of the cell to 80° or 90° C.[1] Below 70° C. hydrogen is deposited and the deposit becomes a black spongy mass. There is no circulation of the electrolyte. The anodes should not contain over 10 percent of impurities, which go into the anode mud as sulfides. The sodium sulfide is used up a little also by oxidation by the air, and must be renewed from time to time. At least 0.6 percent tin as sulfide is added to the bath at the start. The electrolyte is covered with parafine oil to prevent evaporation.

The voltage is 0.2 to 0.3 volt. The anode mud must be scraped from the anodes from time to time. The current density is 0.5 amp./sq. dm., which amounts to 1500 amperes for the whole cell. The current efficiency, calculated for quadrivalent tin, is 98 to 99 percent.

Cathode tin is entirely free from lead, iron, bismuth, silver, copper, phosphorus and arsenic. Antimony, however, is deposited at the usual current densities, but not at very low densities.

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[1] Neumann, Z. Elektroch. **27**, 256 (1921); O. Steiner, Oesterreich. Chem. Ztg. **10**, 207 (1907).

CHAPTER XI

ELECTROLYTIC OXIDATION AND REDUCTION

EVERY electrolytic process consists of an oxidation at the anode and a reduction at the cathode, but those processes in which the products are made only at the anode or at the cathode are called oxidation or reduction processes. Where the reactions at both electrodes are required for the final product, it would not be called an oxidation or reduction process in this narrower sense, unless the product is made by a secondary reaction, such as the oxidation of litharge to peroxide by hypochlorite.

In general, it is necessary to separate the anode and cathode by a diaphragm in making an oxidation or a reduction product, though there are some substances which form a diaphragm at the cathode, such as alkali chromate or calcium chloride, when only a small quantity is in solution. These substances therefore prevent the reduction of the products of oxidation at the anode. There is no substance that prevents oxidation of reduction products as well as chromate prevents reduction, though Turkey red oil in the presence of a calcium salt does so to a certain extent.[1]

Electrolytic Oxidation. — *Regeneration of Chromic Acid.* — Chromic acid is used in the oxidation of anthracene to anthrachinon, and in the oxidation of organic compounds in the manufacture of camphor, organic acids, etc. In some plants the chromic sulfate resulting from the reduction of chromic acid is thrown away, though processes for the regeneration of the acid have been worked out.

The best known of these processes is that of Le Blanc and Reisenegger,[2] which has been operated in a large plant of the Höchst dye works at Gersthofen, Germany. The solution, containing the equivalent of 100 g./l. of chromic oxide as sulfate and 350 g./l. of sulfuric acid is electrolyzed with lead electrodes in a lead-lined

[1] Foerster, *Elektrochemie wässeriger Lösungen*, p. 601 (1922).

[2] U. S. Pat. 630,612 (1899); see also Z. Elektroch. **6**, 256 (1899); Askenasy, *Technische Elektrochemie*, 2, 75 (1916); Billiter, *Die elektrochemischen Verfahren der chemischen Gross-Industrie*, **2**, p. 77 (1911); Lottmoser and Falk, Z. Elektroch. **28**, 366 (1922).

cell divided by a diaphragm into anode and cathode compartments. Chromic acid is formed at the anode, which becomes covered with lead peroxide. This can be represented by the equations:

$$2 \, Cr^{3+} + 3 \, O + 3 \, H_2O = 2 \, Cr^{6+} + 6 \, OH^-,$$
$$2 \, Cr^{6+} + 16 \, OH^- = 2 \, CrO_4^{--} + 8 \, H_2O.$$
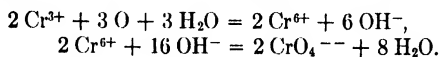
This does not take place on smooth platinum anodes, in spite of the fact that the voltage at a given current density in a chromic acid-sulfuric acid solution is higher on a platinum electrode than on a lead electrode. The presence of a small amount of lead salt in the solution catalyzes the reaction, probably by the formation of lead peroxide, and results in the formation of chromic acid even on a smooth platinum electrode. On platinized platinum the yield is about one third of that on lead anodes, other conditions being equal.[1]

Hydrogen is deposited at the cathode, and sulfuric acid concentrates at the anode and becomes more dilute at the cathode. The oxidized solution is used directly for oxidation and is then circulated to the cathode compartment, where the concentration of sulfuric acid is reduced. It then passes to the anode for oxidation, and repeats the cycle. About 3.5 volts are used per tank and · the current efficiency is 70 to 90 percent.

Chromic acid does not oxidize anthracene rapidly enough to electrolyze the two together between lead electrodes and use the chromic acid as a catalyzer for oxidation.[2]

The Oxidation of Manganate to Permanganate.[3] — Manganate is made by heating potassium hydrate and finely ground manganese dioxide in the presence of oxygen, according to the reaction:

$$MnO_2 + 2 \, KOH + O = K_2MnO_4 + H_2O.$$
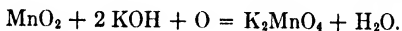
This reaction does not go to completion and there is always unchanged potassium hydrate left over. Schlesinger, Mullinix, and Popoff succeeded in converting 98.4 percent of the manganese

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[1] Mueller and Soller, Z. Elektroch. **11**, 863 (1905).

[2] For the description of another similar process, see McKee and Leo, J. Ind. Eng. Ch. **12**, 16 (1920).

[3] Askenasy and Klonowski, Z. Elektroch. **16**, 104, 170 (1910); Brand and Ramsbottom, J. f. prakt. Ch. **82**, 336 (1910); Dieffenbach, Germ. Pat. 195,523 and 195,524 (1905); Schütz, Z. f. angew. Ch. **24**, II, 1628 (1911); Schlesinger, Mullinix, and Popoff, J. Ind. Eng. Ch. **11**, 317 (1919); Springfield, Chem. Met. Eng. **22**, 1027 (1920); Schlesinger, Jackson, and Cordrey, Ind. Eng. Ch. **15**, 53 (1923).

dioxide to manganate when mixed in the molecular ratio of 2.49 KOH to 1 MnO_2 heated at 450° C., but in some cases the reaction stopped when only 60 percent of the dioxide had been converted. Remoistening and further heating in this case caused further conversion. Sodium hydrate does not give as good a yield as potassium hydrate. Where potassium hydrate gives 85 percent conversion, sodium hydrate gives only 23.4 percent. It is also a peculiarity of this reaction that different samples of dioxide give different results though the content of dioxide is the same.

According to measurements by Askenasy the oxygen dissociation pressure of potassium permanganate is $\frac{1}{5}$ atmosphere at 600° C., so that potassium permanganate could not form above this temperature, if it were not for the fact that a solid solution forms which lowers this dissociation pressure. In making sodium permanganate, in the plants that operated in Southern California during the war the mixture was heated to 980° C.[1]

The manganate is dissolved, filtered, and oxidized to permanganate either electrolytically or by means of chlorine and sulfuric or carbonic acid. Chlorine prevents the formation of manganese dioxide, which takes place when the solution is acidified without chlorine :

$$3 K_2MnO_4 + 2 CO_2 = 2 KMnO_4 + 2 K_2CO_3 + MnO_2,$$
$$2 K_2MnO_4 + Cl_2 = 2 KCl + KMnO_4.$$
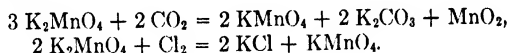
In the electrolysis with a diaphragm, alkali tends to concentrate in the cathode compartment, but it is also produced by oxidation at the anode, as shown by the equation :

$$2 MnO_4^{--} + O + H_2O = MnO_4^- + 2 O H^-.$$
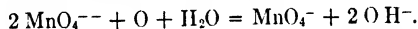
According to Askenasy [2] this electrolysis is also carried out without a diaphragm, as follows : Cathodes consisting of iron rods are placed 2 cm. distant from sheet-iron anodes and are so proportioned that the anodic current density is 9 amp./sq. dm., while the cathodic is 90 amp./sq. dm. At 60° C. this arrangement requires 3 volts across the cell. The yield of potassium permanganate is about 34 kg./kw.-day.

The electrolyte containing permanganate in suspension is cooled and after crystallization, which requires a rather long time, is removed from the crystals and is concentrated in vacuum evaporators.

[1] Springfield, *l.c.*
[2] *Technische Elektrochemie*, **2**, 72 (1916).

Permanganate can also be made by electrolyzing manganese or ferromanganese anodes in a solution of sodium or potassium hydrate as first shown by Lorenz.[1] The iron is oxidized and forms anode mud along with part of the manganese. In potassium hydrate the oxide scale which forms soon insulates the anode so that no more metal goes in solution, but with carbonate this does not happen if the temperature is not allowed to increase much above 40° C. Only about 60 percent of the manganese in the anode goes into the form of permanganate using 75 percent ferromanganese anodes.[2]

The yield in permanganate decreases with the decrease in manganese in the ferromanganese anodes, and under 40 percent there is no yield.[3] The relation between composition and current efficiency is shown by the following figures. These experiments were carried out with 12 percent sodium carbonate at 25° C. at 10 amp./sq. dm.

Percent Anode Composition		Percent Current Efficiency
Mn	Fe	
60.2	31.8	10.34
70.4	22.8	28
80.4	14.4	38.7
89	6.7	45.3
94	0	50.1

The only impurity in the anodes that has a harmful effect is cobalt. A 2-percent content in the anodes prevents the formation of permanganate completely.

The current density has a marked effect on the current efficiency. The efficiency is low at low densities, and rises at first rapidly then more slowly after reaching a current density of 7 to 9 amp./sq. dm. The minimum energy consumption is at 6 amp./sq. dm., but the higher yield obtained at twice this current density more than balances the small increase in cost of energy. With 35 percent current efficiency and 7 volts per cell the yield is about 0.9 kg./kw.-day.

The current efficiency decreases rapidly as the temperature rises. The minimum energy consumption is at 30° C.

[1] Z. anorg. Ch. 12, 393 (1896).
[2] Thompson, Chem. Met. Eng. 21, 680 (1919).
[3] Wilson, Horsch, and Youtz, J. Ind. Eng. Ch. 13, 763 (1921).

This process is much more expensive than the usual one, though it is simpler to carry out.

Chromate can be made from ferrochromium anodes, but this has not yet been as thoroughly investigated as the analogous case of permanganate.

The Oxidation of Potassium Ferrocyanide to Ferricyanide.[1] — Formerly ferricyanide was made by the oxidation of ferrocyanide by chlorine:

$$2 \, K_4Fe(CN)_6 + Cl_2 = 2 \, K_3Fe(CN)_6 + 2 \, KCl,$$
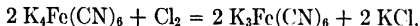
but to some extent electrolytic oxidation has displaced this method, on account of the difficulty of separating the ferricyanide and the potassium chloride. The reaction is:

$$2 \, K_4Fe(CN)_6 + O + H_2O = 2 \, K_3Fe(CN)_6 + 2 \, KOH.$$
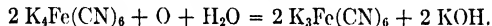
This reaction takes place with a high current efficiency. A diaphragm is necessary to prevent reduction of ferricyanide formed at the anode, as such additions as chromate are not efficient in preventing this reduction.

Ferricyanide is more soluble than ferrocyanide, and ferricyanide would not crystallize from a solution saturated with ferrocyanide and completely oxidized to ferricyanide. An alkaline solution saturated with ferricyanide, however, will dissolve enough ferrocyanide to make nearly 100 percent current efficiency possible, so that by continually adding ferrocyanide to the anode compartment and electrolyzing, solid ferricyanide can be produced in a high degree of purity.

Eventually the anode solution must be freed from the potassium hydrate formed, since only 40 percent of that formed by the oxidation is removed by transference. This cannot be done by evaporation and crystallization of the iron salts without a large loss in ferricyanide by decomposition. Therefore the double salt $K_2CaFe(CN)_6$ is stirred up in the solution and carbon dioxide is passed in at the same time, causing the removal of all hydrate:

$$K_2Ca(CN)_6 + 2 \, KOH + CO_2 = K_4Fe(CN)_6 + CaCO_3 + H_2O,$$
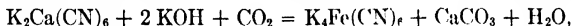
and this solution can then be returned to the anode compartment. Enough water must be added to prevent the precipitation of ferro- and ferricyanide.

The cells used in practice for this oxidation do not seem to have been described.

[1] G. Grube, *Die Elektrolytische Darstellung des Ferricyankaliums,* 1913; Z. Elektroch. **20**, 334 (1914).

The Oxidation of Sulfate to Persulfate. — Persulfuric acid and its salts can be prepared only by electrolysis. They are used in photography as oxidizing agents, and in the production of hydrogen peroxide. Persulfuric acid differs from sulfuric acid in that lead persulfate and barium persulfate are soluble, and in being an oxidizing agent to a limited extent. It oxidizes ferrous sulfate, but does not liberate iodine from an iodide. The relation between hydrogen peroxide, Caro's acid, and persulfuric acid is the following:

$$
\begin{array}{ccc}
\text{OH} & \text{O—SO}_2\text{—OH} & \text{O—SO}_2\text{—OH} \\
| & | & | \\
\text{OH} & \text{OH} & \text{O—SO}_2\text{—OH} \\
\text{Hydrogen} & \text{Caro's Acid} & \text{Persulfuric} \\
\text{Peroxide} & \text{Univalent} & \text{Acid}
\end{array}
$$
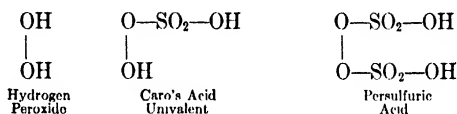
Hydrogen peroxide is made from acid solutions of persulfates by warming with the intermediate formation of Caro's acid:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4, \tag{1}$$

and then

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2. \tag{2}$$
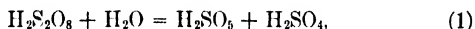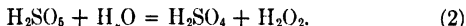
The solution in which these reactions take place must contain between 40 and 58 percent sulfuric acid. Another decomposition to which persulfuric acid and its salts are subject is:

$$M_2S_2O_8 + H_2O = 2\,MHSO_4 + O, \tag{3}$$

but this is very slow at room temperature. All decompositions of persulfates are accelerated at high temperature, consequently the electrolysis has to be carried below 30° C.[1]

The electrolytic oxidation of sulfuric acid or its salts to persulfuric acid or persulfates can be represented by any of the reactions:

$$2\,SO_4^{--} + O + H_2O = S_2O_8^{--} + 2\,OH^-, \tag{4}$$

$$2\,HSO_4^- + O + H_2O = H_2S_2O_8 + 2\,OH^-, \tag{5}$$

$$2\,H_2SO_4 + O + H_2O = H_2S_2O_8 + H_2O, \tag{6}$$

$$2\,HSO_4^- + 2\,F = H_2S_2O_8, \tag{7}$$

$$2\,SO_4^{--} + 2\,F = S_2O_8^{--}. \tag{8}$$
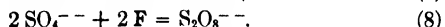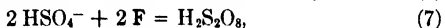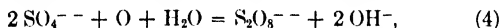
There is no way of telling with certainty which of these reactions take place.[2]

[1] Levi, Z. Elektroch. **9**, 427 (1903).
[2] Friessner, Z. Elektroch. **10**, 287 (1904), believes (7) and (8) do not take place.

Persulfates and persulfuric acid are easily reduced at the cathode, and the anode and cathode must therefore be separated by a diaphragm, or 0.2 percent chromate should be added to prevent reduction. If a diaphragm is used, sulfuric acid is used in the cathode compartment.

The electrolytic oxidation of the sulfate ion is more difficult than the evolution of oxygen [1] and is therefore always accompanied by the evolution of oxygen and ozone. Smooth, ignited platinum anodes give the best results, rough platinum and iridium give poor yields, and palladium or platinized platinum give no yield at all.[2] The presence of ions that make the anode potential more positive, such as chlorine or fluorine, increases the yield.

In adding hydrofluoric acid to the solution there is danger of the formation of salt-crusts at the anodes which destroy the beneficial effect of the fluorine. The cause of this formation is not understood, but the smoother the anode, the less the tendency for the formation to take place. The cation is also of great influence on the yield, since it has been found that the yield is different for different salts of sulfuric acid and for sulfuric acid itself, as is shown in Table 37.[3]

TABLE 37. YIELD OF PERSULFATE IN ELECTROLYSES LASTING 30 TO 40 MIN. AT 6° TO 8° C. C. D. = 50 AMP./SQ. DM. CURRENT = 2 5 AMP. ANODE SOLUTION = 50 CC.

GRAMS H_2SO_4 PER LITER	PERCENT CURRENT EFFICIENCY WHEN THE SO_4 IS PRESENT AS	
	$(NH_4)_2SO_4$	H_2SO_4
80	11.1	0.0
160	37.2	0.5
240	59.1	1.0
320	73.8	4.4
400	82.2	15.3

Potassium and nickel are similar to ammonium in their effects on the yield, but the yields for magnesium and sodium are about the

[1] Elbs and Schoenherr, Z. Elektroch. **1**, 417, 468 (1895); **2**, 245 (1895); Mueller and Schellhaas, *ibid.*, **13**, 257 (1907); Mueller and Friedberger, *ibid.*, **8**, 230 (1902).

[2] Bültemann, Dissertation, Dresden (1905); Foerster, *Electrochemie wässeriger Lösungen*, p. 838 (1922).

[3] Elbs and Schoenherr, Z. Elektroch. **2**, 247 (1905).

same as that with sulfuric acid. The reason for the different yields of different salts of sulfuric acid is not known.

With sulfuric acid the yield shows a maximum at a specific gravity of 1.3 to 1.45. This is due to the fact that while the oxidation to persulfate increases with the concentration of sulfuric acid, the formation of Caro's acid also increases and this lowers the anode potential which in turn lowers efficiency of production of more persulfuric acid, and also uses up that already formed. Caro's acid is reduced at the anode, an exceptional kind of reaction:

$$H_2SO_5 + O = H_2SO_4 + O_2, \tag{9}$$
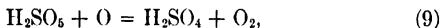
with a simultaneous lowering of the anode potentials. This causes a reduction in the current efficiency in producing persulfuric acid.

On electrolyzing a sufficiently strong sulfuric acid solution, it is found that the current efficiency at first rises, then falls to negative values, and finally approaches slowly a zero value. The anode potential also [1] decreases as the current efficiency falls to zero. This peculiar behavior is due to the reduction of Caro's acid by equation (9), and when the second zero value of current efficiency is reached, the amount of persulfuric acid made equals that destroyed by (9). Figure 75 shows the current yield and the concentrations before and after the first zero value of current efficiency.[2] After passing this zero point, Caro's acid increases at the expense of persulfuric acid and reaches its maximum value when the current efficiency has its largest negative value.

Since persulfuric acid is changed into Caro's acid by a purely chemical reaction, it follows that the concentration of persulfuric acid should increase in proportion as the current concentration increases, as there is then less time for it to change to Caro's acid, and this has been verified experimentally.[3]

The current efficiency reaches a maximum as the current density is increased, because high current density increases the concentration of persulfuric at the anode and consequently increases the amount that changes to Caro's acid by (1).

Increased temperature lowers the anode potential and consequently the current efficiency, and also increases the velocity with which persulfuric acid changes to Caro's acid.

The following are favorable conditions for the production of

[1] Ebbs and Schoenherr, l.c.
[2] H. v. Ferber, Dissertation, Dresden, 1913.
[3] Mueller and Emslander, Z. Elektroch. 18, 752 (1912).

persulfuric acid :[1] anode current density 67 amp./sq. dm., current concentration 55 amp./l. and temperature 3° to 4° C.   These give :
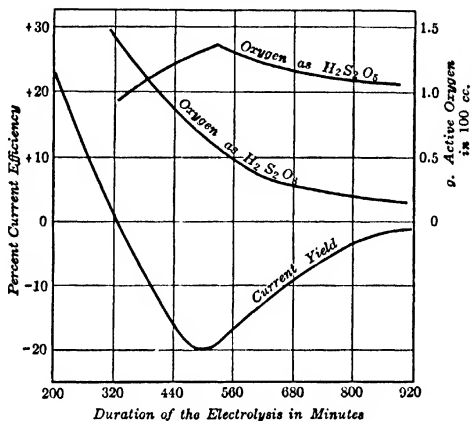
FIG. 75. — ELECTROLYSIS OF 14-n- TO 19-n-H₂SO₄ SOLUTION AT 7° C. ANODE CURRENT DENSITY = 7.5 AMP./SQ. DM. CURRENT CONCENTRATION = 40 AMP./L.

	IN 12-n H₂SO₄	IN 15 n-H₂SO₄
To first zero value of current efficiency;		
g./l. active oxygen	48 to 50	37
Percent current efficiency	37	39
To the point where the current efficiency has just reached 50 percent; g./l. active oxygen	26	24
Percent current efficiency	58	66

As shown above much more favorable yields can be obtained with ammonium sulfate. With a saturated ammonium sulfate solution containing 0.2 percent of potassium chromate, ammonium persulfate can be made continuously, as it is less soluble than ammonium sulfate and crystallizes from the solution. The solution tends to become alkaline as shown by the reaction :

$$2(NH_4)_2SO_4 + O + H_2O = NH_4)_2S_2O_8 + 2\,NH_4OH. \qquad (10)$$

This ammonia has to be neutralized by sulfuric acid since the

[1] Foerster, *Elektrochemie wässeriger Lösungen*, p. 845 (1922).

yield of persulfate decreases in alkaline solution and since ammonia would be lost by oxidation at the anode to nitrogen and nitric acid. The current yield is about 80 percent at 15° to 20° C. at 20 amp./sq. dm. About 8 volts are required with a diaphragm, 6 volts without a diaphragm. With 6 volts and 80 percent current efficiency the yield of ammonium persulfate would be 13.6 kg./kw.-day.

The details of how this electrolysis is carried out in practice are secret. Cells without diaphragms probably use lead water-cooled pipes as cathodes.[1] Chromate does not prevent reduction with lead cathodes,[2] so these must either be wound with asbestos string or high current density must be used.

The relation between cathode current density and current yield in the absence of a diaphragm or chromate in acidified ammonium sulfate solution is as follows : [3]

CATHODE CURRENT DENSITY IN AMP./SQ. DM.	CURRENT YIELD IN PERSULFATE IN PERCENT
10	25
50	50
150	60
300	70

It is important to have the product form large crystals, otherwise they are hard to separate from the mother liquor and are not stable. This is said to be accomplished by the addition of 0.2 percent of a potassium salt.[4]

The oxidation of thiosulfates to tetrathionates, $M_2S_2O_3$ to $M_2S_4O_6$, and sulfites to dithionates, M_2SO_3 to $M_2S_2O_6$, are analogous to the production of persulfates, but they seem to have no technical importance, and will therefore not be discussed.[5] The same is true of percarbonates, $M_2C_2O_6$,[6] which can be made with a current efficiency of 70 percent at − 10° C. Sodium percarbonate is a powerful oxidizing agent and was produced technically for a short while.[7]

[1] Billiter, *Die elektrochemischen Verfahren der chemischen Gross-Industrie*, **2**, 91 (1911).

[2] Foerster, *Elektrochemie wässeriger Lösungen*, p. 599 (1922).

[3] Billiter, *l.c.*, **2**, 91 (1911).

[4] Billiter, *l.c.*, p. 91.

[5] Thatcher, Z. phys. Ch. **47**, 641 (1904), on tetrathionate; Friessner, Z. Elektroch. **10**, 265 (1904), on dithionate.

[6] Constam and Hansen, Z. Elektroch. **3**, 137 (1896), 445 (1897), Germ. Pat. 91,612.

[7] Billiter, *l.c.*, p. 95.

The Electrolytic Oxidation of Sulfur Dioxide. — The use of the large amounts of sulfur dioxide made in roasting sulfur ores might be used to depolarize unattackable anodes in the extraction of copper and in similar operations. This has been studied but apparently has not yet been applied.[1] The dioxide is oxidized to sulfuric acid.

The Luckow Process for White Lead, Lead Chromate, and Lead Dioxide. — In the production of potassium permanganate from ferromanganese an example has been given where the anode itself is oxidized to the desired compound. Another such case is the production of white lead, $2 PbCO_3 \cdot Pb(OH)_2$, from soft lead anodes.[2] If lead anodes were electrolyzed in a solution of sodium carbonate, lead carbonate would stick to the anode, cause the voltage to rise, and the evolution of oxygen and the formation of lead dioxide. This is avoided by using a solution containing only 1.5 percent of alkali salts, 80 to 90 percent of which consists of sodium chlorate, and the rest sodium carbonate. Lead chlorate is formed at the anode and is not precipitated as carbonate until it is so far from the anode that it no longer has a tendency to stick. A low current density is also necessary, about 0.5 amp./sq. dm. The alkali formed at the cathode is neutralized by passing in carbonic acid, but the solution should be slightly alkaline in order to get a basic carbonate. The cathodes are held in linen sacks to prevent blackening the product. Under these conditions the anode remains completely clean and the white lead settles to the bottom of the tank.

It is said that white lead made in this way is too transparent and absorbs too much oil,[3] so it is evidently important to get the right physical state. This is said to have been done by Krejci.[4]

Electrolytic white lead is made at East Chicago by the Anaconda Lead Products Company but no details of the process are available.[5]

By substituting sodium chromate for sodium carbonate in the solution for white lead, lead chromate can be made, but it is mixed with lead dioxide which spoils the color. Lead dioxide can be

[1] M. de K. Thompson, N. J. Thompson, and Sullivan, Met. Chem. Eng. 15, 677 (1916); 18, 178 (1918).
[2] C. Luckow, Germ. Pat. 91,707 (1894); Le Blanc and Bindschedler, Z. Elektroch. 8, 255 (1902); Isenburg, 9, 275 (1903); Min. Ind. 28, 432 (1919).
[3] Miller, J. Phys. Ch. 13, 256 (1909).
[4] Chem. Met. Eng. 22, 531 (1920), editorial.
[5] Min. Ind. 29, 414 (1920).

made by using a 1.5 percent solution of a mixture consisting of 99.5 parts of sodium sulfate and 0.5 part of sodium chloride.

Another method of making lead dioxide is to electrolyze a sodium chloride solution in which lead oxide is suspended.[1] Lead oxide is oxidized by the hypochlorite formed by the electrolysis of the chloride:

$$PbO + NaClO = PbO_2 + NaCl.$$
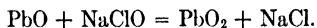
Manganese Dioxide. — This can be made by electrolyzing solutions of manganese sulfate at 0.9 to 1.7 amp./sq. dm. with current efficiencies over 90 percent.[2] This has not yet been applied on a large scale.

Electrolytic Oxidation of Organic Compounds. — Organic substances oxidize only slowly, and part of the oxygen deposited at the anode is liberated as a gas in place of oxidizing the organic substance in solution or suspended in the solution. This results in the anode potential rising to the point where the organic substance is completely destroyed by oxidation to carbonic acid and water. For this reason oxidation is very little used with organic substances. In some cases the anode potential can be prevented from rising to the point at which complete oxidation takes place by adding a salt which catalyzes the oxidation, such as cerium sulfate, or manganese sulfate. Cerium sulfate is especially suited for this purpose, and it has been proposed to use it for the oxidation of anthracene to anthrachinon. A 2-percent solution of ceric sulfate in 20-percent sulfuric acid[3] would be used into which anthracene is stirred. The anode is the lead containing-vessel, the anode current density is 5 amp./sq. dm. at about 3 volts, and the temperature 70° to 90° C. A maximum current efficiency of 80 percent can be obtained,[4] but this decreases as the oxidation proceeds. This method is not used in practice.

Iodoform and bromoform are two of the few examples of the anodic production of organic compounds, and these are made by secondary reactions. Iodoform can be made by the action of iodine on alcohol, acetone, or aldehyde. The chemical method consists in adding iodine to an alkaline solution of alcohol at 60° to 70° C. Iodine forms some hypoiodous acid with the hydroxyl

[1] Germ. Pat. 124,512 (1900).
[2] Van Arsdale and Maier, Tr. Am. Electroch. Soc. **33**, 109 (1918).
[3] Farbwerke vorm. Meister, Lucius & Brüning, Germ. Pat. 152,063 (1902).
[4] Fontana and Perkin, Electroch. Ind. **2**, 249 (1904).

ions and this and free iodine act on alcohol, the result of which can be represented by the equation:

$$CH_3CH_2OH + 3 I_2 + 2 HIO = CHI_3 + CO_2 + H_2O + 5 HI, \quad (1)$$
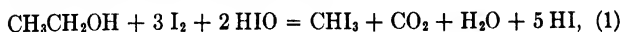
though this is the result of several intermediate reactions. This involves the loss of iodine, and for this reason the electrolytic method has to a large extent displaced the chemical method.

Iodoform is made by electrolyzing at 60° to 70° C. a solution containing 10 to 16 parts of potassium iodide, 5 parts of sodium carbonate, 10 parts of 96-percent alcohol, and 100 parts of water.[1] The current density should be between 1 and 2 amp./sq. dm. at 2 to 2.5 volts. The anode is smooth platinum, and the cathode a lead plate inclosed in parchment to prevent reduction of iodine set free at the anode. Since the electrolytic formation of 2 HIO takes four faradays, and 3 I_2 six faradays, according to equation (1) the theoretical yield in iodoform is 1.47 g./amp. hr. At 2.3 volts the energy yield would be 15.3 kg./kw.-day. The carbonic acid which escapes has to be replaced, otherwise the solution would become more alkaline and the current efficiency would fall, due to the increased formation of iodate in alkaline solution. As iodine is added in the form of potassium iodide the potassium carbonate increases in concentration and has to be removed. Under proper conditions a current efficiency of 80 to 90 percent is obtained.

If acetone is used, the reaction is:[2]

$$CH_3COCH_3 + 3 I_2 = CI_3COCH_3 + 3 HI, \quad (2)$$
$$CI_3COCH_3 + H_2O = CHI_3 + CH_3COOH.$$
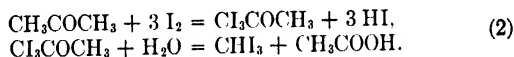
Here the current yield is better, but the solution becomes alkaline more rapidly, and the reaction does not go as well as with alcohol.

Bromoform is made with a good current yield by electrolyzing a solution of potassium bromide in the presence of acetone.[3] The reactions are the same as with iodine. The alkali is neutralized with a vigorous current of carbonic acid so that the solution is slightly acid and the bromoform is colored with free bromine. After the run the bromoform can be decolorized by adding more

[1] Germ. Pat. 29,771 (1884); Elbs and Herz, Z. Elektroch. **4**, 113 (1897); Foerster and Meves, *ibid.*, **4**, 268 (1897).
[2] Abbott, J. Phys. Ch. **7**, 84 (1903); Teeple, J. Am. Ch. Soc. **26**, 170 (1904); Roush, Tr. Am. Electroch. Soc. **8**, 281 (1905).
[3] Coughlin, Am. Ch. J. **27**, 63 (1902); Mueller and Locke, Z. Elektroch. **10**, 409 (1904).

carbonate. A current yield of 90 percent can be obtained by electrolyzing below 30° C. a solution containing 100 g. potassium bromide, 120 g. acid potassium carbonate, 120 g. acetone, and 2 g. potassium chromate per liter, with an anode current density of 10 amp./sq. dm. and a higher cathodic current density.

Chloroform can also be made in the same way,[1] but it is more difficult on account of the volatility of chloroform and on account of the ease with which it is decomposed by alkalinity, or its tendency to be changed to carbon tetrachloride in acid solution.

Electrolytic Reduction. — Electrolytic reduction may be of great importance in applied electrochemistry, but if so, it is strange that not more about it has appeared in print. In very few cases is it possible to give a full account of the way in which a reduction process is carried out technically.

The electrolytic reduction of galena, or lead sulfide, in a sulfuric acid solution was carried out for a while on a large scale at Niagara Falls, but had to be given up eventually on account of the poisonous effect of the hydrogen sulfide produced.

The galena, which had been ground to pass a 40- to 50-mesh sieve, was spread in a layer $\frac{1}{2}$ inch thick and covered with dilute sulfuric acid.[2] The current density was 30 amp./sq. ft., and the current efficiency was about 66 percent.[3] About 97 percent of the lead sulfide was reduced to spongy lead, which was washed free of sulfuric acid, and converted into litharge by roasting.

It is possible that electrolytic reduction is used for the production of salts otherwise difficult to obtain, such as chromous salts.[4] A solution containing 20 g. of chromic sulfate in 100 cc. of 4-normal sulfuric acid is electrolyzed with 3 amp./sq. dm. and a current concentration of 50 amp./l. with vigorous stirring in the cathode compartment. The temperature may increase to 60° C. without harm. The current efficiency at first is 70 to 80 percent but soon falls to low values, and reaches zero when 95 percent of the chromic salt is reduced. By concentrating the solution in a vacuum crystals of $CrSO_4 \cdot 5 H_2O$ are obtained.

[1] Waeser, Chem. Ztg. **34**, 141 (1910); Feyer, Z. Elektroch. **25**, 115 (1919); Roush, Tr. Am. Electroch. Soc. **8**, 281 (1905).

[2] Salom, Trans. Am. Electrochem. Soc. **1**, 87 (1902).

[3] Salom, Trans. Am. Electrochem. Soc. **4**, 101 (1903).

[4] Boehringer & Söhne, Germ. Pat. 115, 463 (1899); Traube and Goodson, B. B. **49**, 1679 (1916).

The lead cathode may be covered with a thin layer of lead sponge,[1] or may be polished and amalgamated.[2] The violet modification of the chloride and sulfate give higher current efficiencies, and the reduction can be carried nearer completion than with the green salts which give complex ions in solution; but the green salts are more easily obtained and are more soluble.

It has been proposed to make the reducing agent sodium hyposulfite, or hydrosulfite, $Na_2S_2O_4$, by electrolytic reduction, in place of reduction with zinc:

$$4\,NaHSO_4 + Zn = Na_2S_2O_4 + Na_2SO_3 + ZnSO_3 + 2\,H_2O.$$
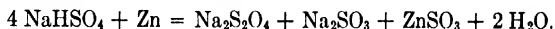
Electrolytic reduction takes place easily:

$$2\,HSO_3^- + 2\,H^+ + 2\,F = S_2O_4^{--} + 2\,H_2O. \qquad (1)$$
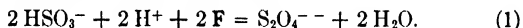
The current efficiency is lowered by the decomposition of the salt according to the reaction:

$$2\,S_2O_4^{--} + H_2O = 2\,HSO_3^- + S_2O_3^{--}, \qquad (2)$$
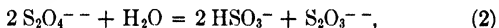
forming the original salt and thiosulfate.[3] As the concentration of hyposulfite becomes higher, its decomposition according to (2) increases until the amount formed equals that decomposed, and the electrolysis apparently then produces only thiosulfate. Therefore, in order to get a high concentration of hyposulfite the current concentration should be high, and the solution should be kept cool. Jellinek prepared a 10-percent hyposulfite solution with 80 percent current efficiency starting with 5-normal acid sodium sulfate and a current concentration of 5 amp./100 cc. The reaction (2) does not go rapidly if the cool solution is dilute in bisulfite.[4] Therefore if the solution contains initially 10 g. bisulfite, and this salt is added as it is used up, a concentrated solution of hyposulfite can be made without a high current concentration.

Electrolytic   Reduction   of   Organic   Compounds.[5] — A large amount of research has been done on the reduction of organic compounds, and this is probably carried out commercially to a

[1] Tafel, Z. phys. Ch. **34**, 190 (1900), finds reductions frequently do not take place well on smooth lead, but that the current efficiency increases when the surface is " formed " or even roughened with sand.

[2] Foerster, *Elektrochemie wasseriger Lösungen*, p. 602 (1922).

[3] Jellinek, Z. Elektroch. **17**, 245 (1911).

[4] Badische Anilin- und Sodafabrik, Germ. Pat. 276,058 (1912).

[5] Haber and Moser, *Die Elektrolytischen Prozesse der organischen Chemie* (1910).

certain extent on high-priced chemicals but is not carried out on a large scale, as far as is known.

One of the best known examples of electrolytic reduction is that of nitrobenzene to aniline or to intermediate compounds. This reduction takes place in steps, as follows:

$$C_6H_5NO_2 \longrightarrow C_6H_5NO \longrightarrow C_6H_5NHOH \longrightarrow C_6H_5NH_2, \quad (1)$$
$$\text{Nitrobenzene} \qquad \text{Nitrosobenzene} \qquad \text{Phenylhydroxylamine} \qquad \text{Aniline}$$
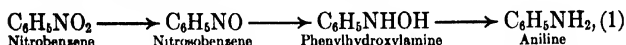
and on strongly reducing cathodes, such as lead, zinc, copper, tin, and mercury the end product is aniline, whether the solution is alkaline or acid. If the cathode is not so strongly reducing, as is the case with nickel, carbon, silver, or platinum, when phenyl-hydroxylamine is formed secondary reactions take place on account of the strongly active nature of this substance, and these reactions are different in alkaline and in acid solutions. The following discussion, therefore, applies only to nickel, carbon, silver, or platinum cathodes. If phenylhydroxylamine is to be made, the solution must be nearly neutral to avoid these secondary reactions. A slight alkalinity or acidity is necessary to give the solution sufficient conductance; a suitable slightly alkaline solution is an alcoholic ammoniacal solution of nitrobenzene containing ammonium chloride.

In acid solution phenylhydroxylamine changes rapidly into para-amidophenol:

$$C_6H_5NHOH = C_6H_4 \Big\langle {{NH_2} \atop {OH}} \qquad (2)$$
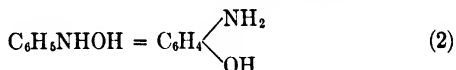
and also reacts with nitrosobenzene:

$$C_6H_5NHOH + C_6H_5NO = C_6H_5N-NC_6H_5 + H_2O. \quad (3)$$
$$\underset{O}{\diagdown\diagup}$$
$$\text{Azoxybenzene}$$
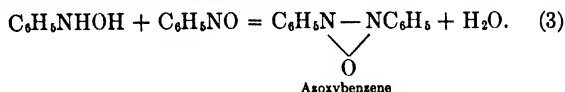
Azoxybenzene is then reduced to hydrazobenzene:

$$C_6H_5NH - NHC_6H_5,$$

which by a rearrangement changes partly to benzidine:

$$NH_2C_6H_4 - C_6H_4NH_2$$
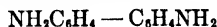
and is partly reduced to aniline. Therefore in an alcoholic sulfuric acid solution the reduction of nitrobenzene gives a mixture of para-amidophenol, benzidine, and aniline. The more concentrated the acid the greater the proportion of para-amidophenol, but the production of benzidine and aniline can not be entirely

prevented.   These reactions can be summarized in the following diagram, where full arrows indicate electrochemical reduction, dotted arrows secondary reactions.

<div align="center">Acid Solution</div>

$$C_6H_5NO_2 \longrightarrow C_6H_5NO \longrightarrow C_6H_5NHOH \longrightarrow C_6H_5NH_2$$

$$C_6H_5NH-NHC_6H_5 \longleftarrow C_6H_5N-NC_6H_5$$

$$\underset{O}{\diagdown\diagup}$$

$$NH_2C_6H_4-C_6H_4NH_2 \qquad CH_6\diagup{NH_2}_{OH}$$
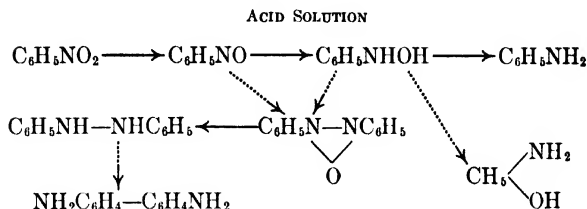
In alkaline solution reaction (3) takes place with great rapidity, and azoxybenzene is then reduced exclusively to hydrazobenzene:

$$C_{12}H_{10}N_2O + 4 H = C_6H_5NH-NHC_6H_5 + H_2O, \qquad (4)$$

which reacts with nitrobenzene as follows:

$$3 C_6H_5NH-NHC_6H_5 + 2 C_6H_5NO_2 = 3 \underset{\text{Azobenzene}}{C_6H_5N=NC_6H_5} +$$

$$\underset{\underset{\text{Azoxybenzene}}{O}}{C_6H_5N-NC_6H_5} + 3 H_2O, (5)$$
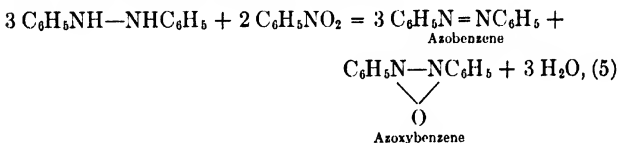
and azobenzene is the final product with the cathodes named above.   The following diagram summarizes the reactions for alkaline solutions:

$$C_6H_5NO_2 \longrightarrow C_6H_5NO \longrightarrow C_6H_5NHOH$$

$$C_6H_5N-NC_6H_5 \longrightarrow C_6H_5NH-NHC_6H_5$$

$$\underset{O}{\diagdown\diagup}$$

$$C_6H_5N=NC_6H_5$$
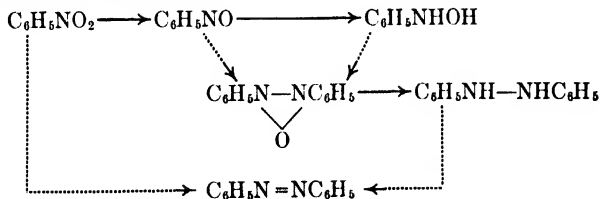
Similar reactions take place with many substitution products of nitrobenzene.

As to the application of these reactions, not much information is available.   During the war the Eastman Kodak Company attempted the electrolytic production of para-aminophenol. Platinum cathodes 25.4 cm. wide, 30 cm. long, and 0.075 mm.

thick were used, and platinum anodes of a small area. Lead anodes were found to [1] favor the formation of aniline. The cells were glazed earthenware and the diaphragms were thin porous porcelain, 12 in. square, held in place by sulfur seals. Forty such cells were set up in banks of ten connected in series; cooling to 30° C. was effected by placing the cells in a tank of water with cooling coils through which brine circulated. The catholyte consisted of 540 cc. of nitrobenzene and 1800 cc. of 91-percent sulfuric acid, while the anode compartments were filled with sulfuric acid of 1.75 specific gravity. A current of 60 amp. (6 amp./sq. dm.) was passed for 24 hours, at 8 volts, 4 of which were due to the diaphragm. The forty cells produced 57 to 69 kg. of para-aminophenol hydrochloride per week at a current efficiency of 25 percent, and a yield of 0.9 to 1.2 kg./kw.-day The chief expenses were the sulfuric acid and the labor. The cost with this equipment was too high to compete with any chemical method and the process was given up, and the cells were used for the preparation of ammonium persulfate.

It is rumored that in Germany nitrobenzene is reduced to aniline in the cathode compartments of cells for chlorine and caustic. This would probably also lower the voltage required by these cells.[2]

[1] McDaniel, Schneider, and Ballard, Tr. Am. Electroch Soc. **39**, 441 (1921).
[2] For a discussion of the industrial electrolytic preparation of organic chemicals, see Thatcher, Tr. Am. Electroch. Soc. **36**, 337 (1919); and Strachan, J. Ind. Eng. Ch. **14**, 910 (1922).

CHAPTER XII

THE ELECTROLYSIS OF ALKALI HALIDES

Theoretical Discussion. — *The Chemical Action of the Halogens on Alkali Hydrate.* — The electrolysis of sodium and potassium chlorides is one of the largest electrochemical industries that is carried out in aqueous solution ; the electrolysis of the other halides is comparatively unimportant. Chlorine and sodium hydrate, hypochlorite, chlorate, or perchlorate may be produced from sodium chloride, depending on the conditions of the electrolysis.

The first products obtained on electrolyzing the solution of an alkali chloride are chlorine at the anode and alkali hydrate at the cathode. If these two primary products are the ones desired, they must not be allowed to mix, while if hyperchlorite, chlorate, or perchlorate is desired, the chlorine and hydrate must be allowed to react with each other. Before describing the electrolysis of the alkali halides a brief account of the purely chemical reactions that take place between the halogens and hydroxyl ions will be given.

When fluorine acts on hydroxyl ions it discharges an equivalent number of hydroxyl ions just as zinc ions replace those of copper :

$$F_2 + 2 OH^- = 2 F^- + H_2O + O, \tag{1}$$

and the oxygen is partly in form of ozone. The electrolytic solution pressure of fluorine is so great that reaction (1) takes place in any aqueous solution, whatever the concentration of the hydroxyl ions. With the other halogens the reaction is different :

$$X_2 + OH^- = X^- + XOH, \tag{2}$$

but in a neutral or acid solution reaction (2) takes place so slowly that these halogens can be obtained in the free state. If all of X is to react with hydroxyl ions the hydroxyl ion concentration must be a little greater than its value in pure water, and in this case the acid XOH is neutralized :

$$XOH + OH^- = XO^- + H_2O, \tag{3}$$

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so that the total reaction of chlorine, bromine, and iodine on hydroxyl ions is:

$$X_2 + 2\,NaOH = NaX + NaOX + H_2O. \qquad (4)$$

With chlorine (4) goes to completion from left to right while with bromine and iodine there is an appreciable amount left uncombined at equilibrium, when mixed with equivalent amounts of hydrate. Hypochlorite is not stable, but tends to change to chlorate in the presence of even very minute amounts of acid:

$$2\,HOCl + NaOCl = NaClO_3 + 2\,HCl, \qquad (5)$$

and the hydrochloric acid set free by reaction (5) sets free more hypochlorous acid, so that the reaction continues till all hypochlorite is changed to chlorate. Hypobromites change according to (5) with 100 times the velocity of hypochlorites, and hypoiodites with a velocity too rapid to measure.

In alkaline solution hypochlorite and hypobromite are much more stable than in acid, and may be kept unchanged for days, but eventually are changed to chlorate or bromate. With hypochlorite this takes place in two steps:

$$2\,NaClO = NaClO_2 + NaCl, \qquad (6)$$

$$NaClO_2 + NaClO = NaClO_3 + NaCl.[1] \qquad (7)$$

Reaction (7) is about 36 times as rapid as (6). Here, as in acid solution, bromate is formed more rapidly than chlorate, and iodate so rapidly that in a short time no hypoiodite is left. Reactions (6) and (7) are also accompanied to a slight extent by the following:

$$2\,NaOX = O_2 + 2\,NaX. \qquad (8)$$

This is catalyzed by the presence of oxides of cobalt, nickel, copper, iron, etc., and by platinum black. Cobalt oxide is an especially active catalyst for this reaction, and causes (8) to go so rapidly that no chlorate is formed.[2]

Perchlorate cannot be formed by the further action of chlorine on chlorate, but is produced by the decomposition of chlorate, as will be explained below.

The Electrolysis of Alkali Halides on Smooth Platinum Electrodes without a Diaphragm. — If a concentrated neutral solution of alkali chloride is electrolyzed between smooth platinum electrodes,

[1] Foerster, Z. Elektroch. **23**, 137 (1917).
[2] Foerster and Jorre, J. f. prakt. Ch. **59**, 53 (1899); Foerster, *ibid.*, **63**, 141 (1901).

the alkali is deposited on the cathode and reacts with the water according to the equation:

$$2\,\text{Na} + 2\,\text{H}_2\text{O} = 2\,\text{NaOH} + \text{H}_2. \tag{9}$$

The hydrogen produced escapes, unless it is used up in reducing some substance in the solution. On the anode, chlorine is liberated from the ionic form to free chlorine, as follows:

$$2\,\text{Cl}^- + 2\,\text{F} = \text{Cl}_2. \tag{10}$$

The liberated chlorine partly dissolves in the water and at first partially escapes from the solution. Soon, however, the alkali hydrate produced at the cathode and the dissolved chlorine are brought together by the stirring produced by the escaping hydrogen, and after this no more chlorine escapes from the solution. Chlorine and alkali hydrate are produced in equivalent quantities, so that the equation (4),

$$\text{Cl}_2 + 2\,\text{NaOH} = \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O},$$
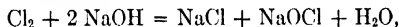
is practically quantitative. It is evident that only 50 percent of the chlorine liberated is obtained in the form of hypochlorite, but this chlorine is equivalent to twice as much free chlorine because of the reaction:

$$\text{HCl} + \text{HOCl} = \text{H}_2\text{O} + \text{Cl}_2. \tag{11}$$

A solution containing one formula weight of hypochlorite contains therefore 70 g. of active chlorine. As the electrolysis proceeds, the hypochlorite becomes more and more concentrated, until finally a limiting concentration is reached, whose value is determined by a number of factors, such as the material of the anode, the current densities on the anode and cathode, the temperature, and the
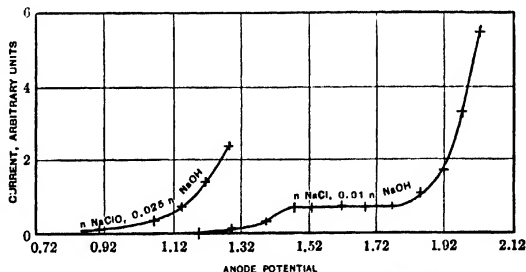
FIG. 76. — ANODE POTENTIALS AND CURRENT DENSITIES IN SOLUTIONS OF SODIUM HYPOCHLORITE AND OF SODIUM CHLORIDE

original concentration of the chloride solution. This is due to the fact that the hypochlorite, almost from the start, is also decomposed by the current, and this decomposition increases as the concentration of the hypochlorite increases, until the amount decomposed is just equal to the amount produced. This decomposition takes place in two ways; at the cathode the hypochlorite is reduced by the hydrogen as follows:

$$NaOCl + H_2 = H_2O + NaCl, \tag{12}$$
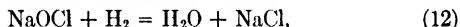
and at the anode the hypochlorite ion is liberated, since it is more easily discharged than the chlorine ion,[1] as shown in Figure 76, and reacts with the water, producing chlorate and oxygen according to the following reaction : [2]

$$6 F + 6 ClO^- + 3 H_2O = 2 ClO_3^- + 4 Cl^- + 6 H^+ + 1\tfrac{1}{2} O_2. \tag{13}$$
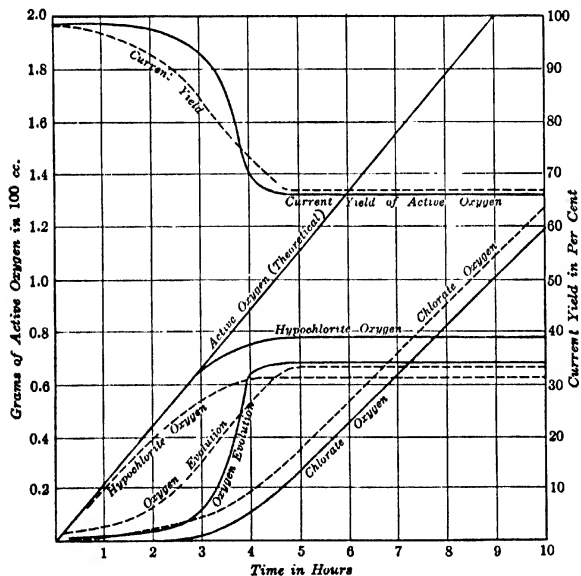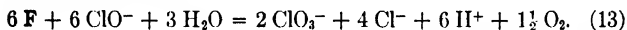
FIG. 77. — ELECTROLYTIC PRODUCTION OF SODIUM HYPOCHLORITE IN NEUTRAL, 5.1-NORMAL SODIUM CHLORIDE SOLUTIONS CONTAINING 0.2 PERCENT OF POTASSIUM CHROMATE. FULL LINES: PLATINIZED PLATINUM ANODES; DOTTED LINES: SMOOTH PLATINUM ANODES

[1] Foerster and Mueller, Z. f. Elektroch. **8**, 634 (1902).
[2] Foerster and Mueller, Z. f. Elektroch. **8**, 667 (1902).

This has been called the *anode chlorate formation*, since it takes place only on the anode and not throughout the solution.

The graphs in Figure 77 show the course of the electrolysis of 220 cc. of a 5.1-n solution of sodium chloride containing 0.2 percent of potassium chromate. The electrolysis was carried out with 2 amp. (anodic current density, 6.7 amp./sq. dm.) at 12° to 13° C.[1] These show that at first only hypochlorite is produced, and that the production of hypochlorite decreases as the oxygen evolution begins. Finally the chlorate reaches a constant concentration, after which only chlorate is formed. The yield on platinized platinum is higher than on smooth, because chlorine is liberated on platinized platinum at about 0.6 volt lower electrode potential than on smooth platinum, so that there is less hypochlorite discharged and consequently a better yield. Reduction is completely prevented by the potassium chromate, and the only loss in hypochlorite is due to its change to chlorate by reaction (13). It is to be noticed that when all the hypochlorite formed by (4) is decomposed by (13) the current efficiency of producing chlorate oxygen is $66\frac{2}{3}$ percent, since while 12 equivalents of chlorate oxygen are produced 6 equivalents escape into the air. This is also shown by the curves. This is therefore not the best way to make chlorate; but the solution should be slightly acid so that chlorate will form by (5)[2] without further electrolysis. An alkali bicarbonate or acid potassium fluoride (KHF_2) may be used for this purpose. If it were not for the addition of the potassium chromate, the current efficiency would be much below $66\frac{2}{3}$ percent, on account of the reduction of hypochlorite.[3]

The principal factors that affect the current efficiency and the maximum concentration in the electrolytic production of hypochlorite are:

(1) the temperature, (2) the concentration, (3) the alkalinity, (4) the kind of electrode, (5) the current density, and (6) whether or not the solution is stirred.

As the temperature increases, the maximum concentration of hypochloride decreases, since an increase in temperature causes the equilibrium (2) to be displaced in favor of HOCl, so that the

[1] Foerster, *Elektrochemie wässeriger Lösungen*, p. 672 (1922).

[2] Foerster and Mueller, Z. Elektroch. **8**, 12 (1902); **10**, 731 (1904).

[3] The effect of chromate was discovered by Imhoff, Germ. Pat. 110,505 (1898); the mechanism was explained by Mueller, as consisting in the formation of a thin diaphragm of an oxide of chromium. Z. Elektroch, **5**, 469 (1899); **7**, 398 (1900); **8**, 909 (1902).

hypochlorite anion's concentration is increased at the anode, and it is therefore discharged as rapidly as formed at an earlier stage in the electrolysis. The higher the concentration the greater the maximum concentration of hypochlorite, and the greater the current efficiency for a given concentration of hypochlorite. The best results for hypochlorite are obtained in neutral solutions for, if acid, chlorate is formed by reaction (5) and in alkaline solutions the maximum concentration of hypochlorite decreases with increase in alkalinity as shown in Figure 78.[1]

FIG. 78. — EFFECT OF ALKALINITY ON ELECTROLYTIC PRODUCTION OF SODIUM HYPOCHLORITE. SOLUTIONS CONTAINED 200 G./L. OF SODIUM CHLORIDE. DURATION OF ELECTROLYSES: 1 HR. ANODE CURRENT DENSITY: 4 AMP./SQ. DM.

A neutral solution may become acid due to the carbonic acid absorbed from the air, which reacts as follows:

$$NaOCl + CO_2 = NaHCO_3 + HOCl \qquad (14)$$
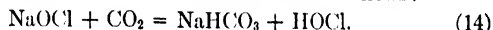
The maximum concentration of hypochlorite in alkaline solution is increased by rise in temperature as shown in Figure 79 in place of being decreased as in neutral solutions, because at higher temperatures the chemical polarization for the discharge of oxygen is lowered and relatively less hypochlorite anions are discharged and consequently less chlorate is formed.

On graphite electrodes the results of chloride electrolysis are somewhat different from those on platinum because graphite is porous and electrolysis takes place partly in the pores where the solution becomes more dilute than in the
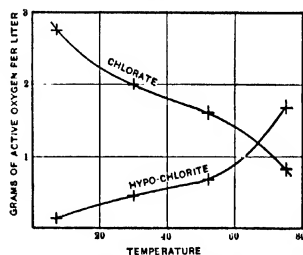
FIG. 79. — EFFECT OF TEMPERATURE ON ELECTROLYTIC PRODUCTION OF SODIUM HYPOCHLORITE IN ALKALINE SOLUTIONS CONTAINING 200 G./L. OF SODIUM CHLORIDE AND 40 G./L. OF SODIUM HYDRATE. ANODE CURRENT DENSITY: 4.5 AMP./SQ. DM.

[1] Mueller, Z. Elektroch. 6, 20 (1899); Z. anorg. Ch. 22, 72 (1900); Foerster and Mueller, Z. Elektroch. 9, 205 (1903).

body of the solution. These electrodes, therefore, produce the same effects as though the solution were more dilute. If the solution becomes so dilute that oxygen is liberated, this forms carbonic acid to some extent and gives the solution a slight acidity, which changes the hypochlorite to chlorate.[1]

A high current density at the anode gives less opportunity for the discharge of hypochlorite anions and therefore improves the current efficiency for hypochlorite. In the same way a high cathode current density lessens reduction when it is not prevented entirely by chromate. Stirring is harmful to the yield of hypochlorite[2] because it brings hypochlorite in contact with the anode where it can be discharged. An undisturbed diffusion layer should be allowed to form at the anode, to obtain the best yield.

Taking the decomposition voltage of 4-n sodium chloride as 2.2 volts on platinized platinum and 100 percent current efficiency, the maximum energy yield in active chlorine in hypochlorite is 14.5 kg./kw.-day. On smooth platinum the decomposition voltage would be about 0.5 volt higher. A solution containing 18 g. active chlorine per liter can be made with 85 percent of the above efficiency with platinized platinum from 5-n sodium chloride, at 11.5 amp./sq. dm., while with smooth platinum 15 g./l. are produced with 46 percent of this efficiency.[3]

The maximum concentration of hypochlorite increases steadily with the anode current density. At 1430 amp./sq. dm., 88 g. of active chlorine per liter can be made, but with very poor energy efficiency. The current efficiency, of course, depends on the concentration of hypochlorite.

If chlorate is made in a slightly acid solution at a high temperature the concentration of hypochlorite remains at a low value, the loss of oxygen due to its discharge is also low, and the current efficiency may be 85 percent or more. The following data are easily calculated:

	KClO$_3$	NaClO$_3$
Grams per amp.-hr. at 100 percent current efficiency	0.764	0.664
Kg./kw.-day at 85 percent current efficiency and 4.5 volts per cell	3.46	3.08

The production of perchlorate[4] takes place with the best current

[1] Sproesser, Z. Elektroch. 7, 971, 987, 1012, 1027, 1071, 1083 (1901).

[2] Prausnitz, Z. Elektroch. 18, 1025 (1912).

[3] Foerster, *Elektrochemie wässeriger Lösungen*, p. 691 (1922).

[4] Haber and Grinberg, Z. anorg. Ch. 16, 225 (1897); Foerster, Z. Elektroch. 4, 386 (1898); Winteler, *ibid.*, 5, 49 and 217 (1899); 7, 635 (1901); Oechsli, *ibid.*, 9, 807 (1903); Blau and Weigand, *ibid.*, 27, 1 (1921).

efficiency at high current density, at low temperature, and high anode potential, consequently smooth platinum anodes should be used. Alkalinity is harmful but the concentration of chlorate is of little importance.[1]

The effects of temperature and current density are shown in Figure 80. From this it is evident that the bad effect of high temperature can be offset to a large extent by increasing the current density. Thus J. G. Williams[2] has shown that by using 45 to 50 amp./sq. dm., and 600 to 700 g./l. of sodium chlorate a current efficiency of 85 percent is obtained at 60° C. and the energy efficiency is 7 kg./kw.-day at 41.5° C., 8 kg./kw. day at 60° C.

The disadvantage of the high temperature is that not all of the chlorate can be changed to perchlorate as can be done at low temperature, and there is some reduction to chloride.
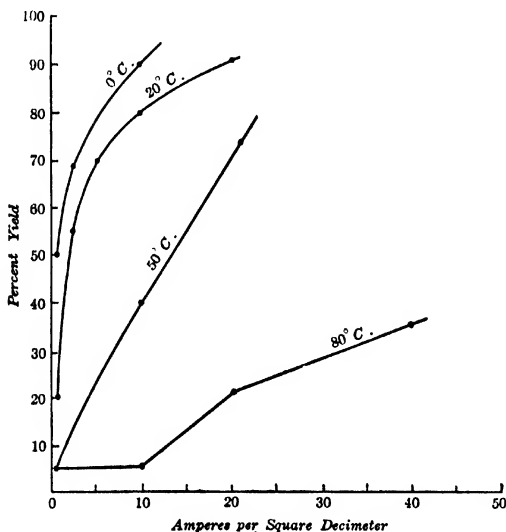
FIG. 80. — EFFECTS OF TEMPERATURE AND CURRENT DENSITY
ON THE PRODUCTION OF PERCHLORATE

[1] Winteler, Z. Elektroch. 7, 635 (1901).
[2] Tr. Faraday Soc. 15, 134 (1920); Engineering, 108, 827 (1919). Also Knibbs, Tr. Faraday Soc. 16, 430 (1920).

Platinum or platinum-iridium are the only anode materials that can be used for making perchlorate. Graphite would be rapidly oxidized and magnetite has not a high enough overvoltage to produce chlorate.[1] The oxygen overvoltage of magnetite anodes in normal sodium chlorate is from 0.4 to 0.6 volt lower than on smooth platinum.

The production of perchlorates does not take place until practically all chloride is removed, because of the greater electrode potential difference required for the discharge of the chlorate ion. A very concentrated solution of chloric acid is thus formed at the anode which decomposes of itself into perchlorate. The chemical decomposition of chloric acid is as follows:

$$2\ HClO_3 = HClO_4 + HClO_2, \tag{15}$$

$$HClO_3 + HClO_2 = H_2O + 2\ ClO_2,$$
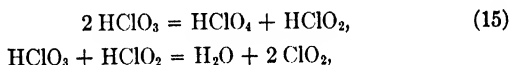
and the corresponding electrolytic reactions are:

$$2\ ClO_3^- + H_2O + 2\ F = HClO_4 + HClO_2 + O, \tag{16}$$

$$HClO_2 + O = HClO_3.$$
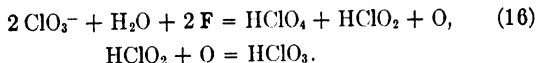
It is also possible that at the high electrode potential of smooth platinum electrolytic oxygen can oxidize chlorate directly to perchlorate.[2]

Another suggestion is that perchlorate is formed as follows:[3]

$$2\ ClO_3^- + O = Cl_2O_7^{--},$$

$$Cl_2O_7 + H_2O = 2\ HClO_4. \tag{17}$$
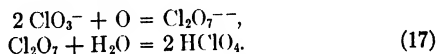
The oxidation of hydrochloric acid to perchloric acid takes place in the presence of hydrochloric acid,[4] thus differing from chlorides of the alkali metals, which are not oxidized to perchlorates in the presence of chloride. A 0.5-n hydrochloric acid solution is electrolyzed with platinum anodes at 18° C. and an anodic current density of 16 amp./sq. dm. and 8 volts. The electrolytic cell is of silver and also forms the cathode. The volume of the cell was about 2.9 l., and the electrolyte circulated at the rate of 2.5 to 3 l./hr.

The following results were obtained:

[1] Howard, Tr. Am. Electroch. Soc. **43**, 51 (1923).
[2] Bennett and Mack, Tr. Am. Electroch. Soc. **29**, 323 (1916).
[3] Campbell, Doctor's thesis, Mass. Inst. of Tech. (1921).
[4] Goodwin and Walker, Tr. Am. Electroch. Soc. **40**, 157 (1921).

CONCENTRATIONS IN NORMALITY

	INITIAL HCL	FINAL HCL	FINAL HCLO₃	FINAL HCLO₄
First passage through cell	0.5	0.0179	0.0255	0.0738
Second passage through cell	0.5	0.0171	0.0089	0.2015
Third passage through cell	0.5	0.01117	0.0078	0.286

This process has a low efficiency both as to material and power, as only 10 percent of the acid is oxidized to perchlorate, 75 percent of the chlorine is evolved as gas, and the energy yield is about 0.92 kg. of 60-percent acid per kilowatt-day. The concentration of hydrochloric acid cannot be made higher at the start because the current efficiency would be even lower. The perchloric acid is concentrated to 60-percent by evaporation and is then distilled. A few hundred pounds a year is made in this way for analytical purposed by the Genesee Chemical Co., Batavia, New York.

Graphs similar to those for chloride electrolysis are found for bromide [1] and for iodide [2] electrolysis. The principal points of difference from the electrolysis of chlorides are that a more concentrated hypobromite solution can be made than of hypochlorite, and bromate is made by the direct oxidation of hypobromite:

$$BrO^- + 2\,O = BrO_3^-, \text{ and by } 3\,NaBrO = NaBrO_3 + 2\,NaBr,$$
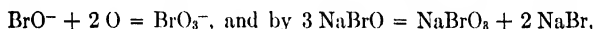
but not by the discharge of the hypobromite anion. Only very dilute hypoiodite solutions can be made, on account of its rapid purely chemical change to iodate.

Perbromates are unknown. Periodate can be made by electrolyzing iodate in alkaline solution in the presence of chromate, with the change of all iodate to periodate. If a diaphragm or chromate is not used, iodate is reduced to iodide, and the iodide is oxidized at the anode, so that the amount of iodide and iodate in solution reaches a constant value.[3] This solution is unique in that electrolysis takes place with unattackable electrodes without gas evolution. In neutral or acid solution a good yield of periodate can be obtained with lead dioxide anodes.

The analysis of the gas coming from a cell in which an alkali

[1] Pauli, Z. Elektroch. **3**, 474 (1807); Kretzschmar, *ibid.*, **10**, 789 (1904); Foerster and Yamazaki, *ibid.*, **16**, 321 (1910).

[2] Foerster and Gyr, Z. Elektroch. **9**, 215 (1903); Herrschel, Dissertation, Leipzig (1912); Foerster, Z. Elektroch. **22**, 89 (1916).

[3] Mueller, Z. Elektroch., **7**, 509 (1901); **10**, 49 (1904).

halide is electrolyzed has been used extensively to follow the reactions taking place in the cell. This is illustrated by the following example.[1]

The cell containing the chloride solution was connected in series with a water coulometer. During a given time, at the beginning of the electrolysis, 60 cubic centimeters of gas were evolved from the coulometer and 32 cubic centimeters from the chloride solution. In the coulometer, 40 cubic centimeters of the gas must have been hydrogen. By analysis it was found that the gas from the chloride solution had the following composition: 30 cubic centimeters of hydrogen, 1.6 of oxygen, and 0.4 of chlorine. This shows a difference in the amount of hydrogen in the two cells of 10 cubic centimeters. This amount must therefore have been used to reduce the hypochlorite already formed. Since 40 cubic centimeters of hydrogen represents the total current, or 100 percent, the loss of current due to reduction was $100 \times \frac{10}{40} = 25$ percent.

The loss due to the evolution of chlorine equals $100 \times \frac{0.4}{40}$, or 1 percent. The 1.6 cubic centimeters of oxygen are equivalent to twice as much hydrogen, or 3.2 cubic centimeters. The loss of current by changing hypochlorite to chlorate was therefore $100 \times \frac{3.2}{40} = 8$ percent. The current used to produce hypochlorite is proportional to the amount of hydrogen evolved from the chloride solution, diminished by the quantity of chlorine evolved, and twice the amount of oxygen: $30 - (3.2 + 0.4) = 26.4$ cubic centimeters. The current yield is therefore $100 \times \frac{26.4}{40} = 66$ percent. This, of course, means that 66 percent of the current produces hypochlorite according to equation (4):

$$Cl_2 + 2\,NaOH = NaCl + NaOCl + H_2O.$$

The rest of the current destroys hypochlorite already produced, or produces chlorine which escapes from the cell. Chlorine is evolved, however, only at the very beginning of the electrolysis, before the hydrate and chlorine have had time to mix. The following table sums up the results of this calculation:

	PERCENT
Current used to produce hypochlorite	66
Current used to reduce hypochlorite	25
Current loss by changing hypochlorite to chlorate	8
Current loss due to evolution of chlorine	1
	100

[1] F. Oettel, Z. f. Elektroch. 1, 354 (1894).

The Electrolysis of Alkali Chlorides for Producing Alkali and Chlorine. — If the object in electrolyzing an alkali chloride is to produce an alkali hydrate and chlorine, the anode and cathode must be separated in order to prevent the hydrate and chlorine from mixing. There are four ways in which the separation of the hydrate and chlorine is effected. These are: (1) by the use of a diaphragm; (2) by inclosing the anode in an inverted, non-conducting belljar with the cathode outside; (3) by charging a mercury cathode with sodium in an electrolytic cell and decomposing the sodium amalgam with water in another vessel; and (4) by a mercury diaphragm, which acts as an intermediate electrode.

(1) Since electrolytic conduction takes place through a diaphragm, it is evident that the separation in this case will not be perfect, for the diaphragm prevents only mechanical mixing. The hydroxyl ions will migrate through the diaphragm and react with the chlorine in the same way as described above. The hydroxyl ions also pass through the diaphragm by ordinary diffusion. Electro-osmosis, on the other hand, drives the liquid through the diaphragm from the anode to the cathode, and therefore opposes the diffusion and migration of the hydroxyl ions.[1]

Current Efficiency in Hydrate. — If diffusion and osmosis just balance each other, the yield in hydrate can be calculated as follows.[1] Before sodium hydroxide appears at the diaphragm, the sodium chloride transports all of the electricity, but when the hydrate is mixed with the chloride, the hydrate will also take part in carrying the current through the diaphragm. If the fraction of the current carried by the hydrate is x, that carried by the chloride will be $1 - x$, and x and $1 - x$ must be proportional to the conductivities of the hydrate and of the chloride in the solution. If L_1 is the conductivity of the chloride and L_2 that of the hydrate, this is expressed by the equation:

$$\frac{1 - x}{x} = \frac{L_1}{L_2} = \frac{C_1\gamma_1\lambda'_\infty}{C_2\gamma_2\lambda''_\infty}, \tag{18}$$

in which C_1 and C_2 are the concentrations in mols per liter, γ_1 and γ_2 are the dissociations, and λ'_∞ and λ''_∞ are the conductivities at infinite dilution, of the chloride and hydrate respectively. For potassium chloride and potassium hydrate, $\dfrac{\lambda'_\infty}{\lambda''_\infty} = 0.545$, and for

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[1] Foerster and Jorre, Z. f. anorg. Ch. **23**, 158 (1899).

sodium chloride and sodium hydrate, the value of this fraction is 0.502.   For potassium chloride and potassium hydrate, equation (18) becomes

$$\frac{1 - x'}{x'} = 0.545 \frac{C_1 \gamma_1}{C_2 \gamma_2},$$

or

$$x' = \frac{1}{1 + 0.545 \dfrac{C_1 \gamma_1}{C_2 \gamma_2}}, \qquad (19)$$

and for sodium hydrate and sodium chloride,

$$x'' = \frac{1}{1 + 0.502 \dfrac{C_1 \gamma_1}{C_2 \gamma_2}} \qquad (20)$$

Now if all of the current were carried by the hydrate, and if n were its transference number, n equivalents of hydrate would pass out of the cathode compartment through the diaphragm in the same time that one equivalent is produced.   In this case the yield in hydrate would be

$$A = 100 \, (1 - n) \text{ percent.}$$

The hydrate carries only a fraction of the current, however, equal to x.   The yield is therefore

$$A = 100 \, (1 - nx) \text{ percent.}$$

The transference number, n, for potassium hydrate is 0.74, and for sodium hydrate it is 0.83.   Substituting the values for x in equations (19) and (20), and the values for n just given, for potassium,

$$A_K = 100 \left[1 - \frac{0.74}{1 + 0.545 \dfrac{C_1 \gamma_1}{C_2 \gamma_2}} \right], \qquad (21)$$

and for sodium,

$$A_{Na} = 100 \left[1 - \frac{0.83}{1 + 0.502 \dfrac{C_1 \gamma_1}{C_2 \gamma_2}} \right]. \qquad (22)$$

It is evident from these equations that, as the hydrate becomes more concentrated, the fraction in the parenthesis becomes greater, which reduces the value of A.   Table 38 shows how the yield

decreases as the concentration increases.[1] The electrolysis was carried out with 700 cubic centimeters of a solution containing 200 grams of potassium chloride per liter in the cathode compartment, and 500 cubic centimeters of the same solution in the anode compartment. The electrodes were platinum, and the diaphragm was of Pukall clay. The current density on the diaphragm was 1.6 ampere per square centimeter. The yield which was being obtained at the end of each period was calculated by formula (21) from the values of the concentrations of chloride and hydrate existing at the end of the period, assuming that the dissociation of the hydrate and chloride are equal.

TABLE 38

TIME	GRAMS OF KOH PRODUCED	GRAMS Cu DEPOSITED IN COULOMETER	MEAN CURRENT YIELD FOR THE CORRESPONDING 2 HR.	EQUIVALENTS PER LITER IN THE CATHODE COMPARTMENT OF		COMPUTED CURRENT YIELD, PERCENT
				Chloride	Hydrate	
1st 2 hr.	17.78	11.47	88.08	2.382	0.418	81.3
2d 2 hr.	14.29	11.71	69.30	2.224	0.754	70.4
3d 2 hr.	13.60	11.61	66.50	2.096	1.071	62.6
4th 2 hr.	11.11	11.85	58.02	2.066	1.331	55.0

It will be seen from the numerical values in equations (21) and (22) that the yield of hydrate with potassium chloride will be better than with sodium chloride, at 18°, to which temperature these numbers apply. Since, however, all transference numbers approach the limit 0.5 as the temperature is raised, these formulæ indicate that the yield in hydrate would increase with the temperature and approach the same value for sodium and potassium chlorides. Since a rise in the temperature also increases the diffusion, the increase in the yield which would be predicted by the formula would be somewhat too large.

Current Efficiency in Chlorine. — Since the hydroxyl ions that migrate to the anode compartment find an excess of chlorine, hypochlorous acid will be produced according to the equation:

$$Cl_2 + OH^- = HOCl + Cl^-.$$
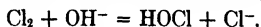
If this proceeded indefinitely, the loss in chlorine would be twice the loss in hydrate. On platinum anodes this has been found to be true in the first stages of the electrolysis.[2] As the hypochlorous

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[1] Foerster and Jorre, Z. f. anorg. Ch. **23**, 193 (1899).
[2] Foerster and Jorre, *l.c.*; Briner, J. Chim. Phys. **5**, 398 (1907).

acid becomes more concentrated, compared to the chlorine, it will be neutralized by the hydroxyl ions coming through the diaphragm, forming hypochlorite. This is then immediately oxidized to chlorate by the excess of hypochlorous acid, according to equation (5). Consequently, no hypochlorite is found in the anode compartment.

The process in the anode compartment is essentially the same when carbon anodes are substituted for platinum, with the exception, of course, that carbon dioxide, as well as oxygen, is produced. On magnetite anodes there is more oxygen evolution and less chlorate formation than on platinum, since magnetite catalyzes the reaction $2 ClO^- = O_2 + 2 Cl^-$ and decreases the concentration of hypochlorite and consequently the anode chlorate formation.

(2) The principle of the *belljar process* is illustrated in Figure 81. The anode is placed in a belljar and the cathode outside. The current flows under the lower rim of the belljar from anode to cathode. Chlorine is evolved and passes out through the tube in the top of the belljar, while hydrate is formed on the cathode. The process that takes place in this cell is very similar to that in a cell with a diaphragm.[1]   At first the solution in the anode compartment is divided into three sharply defined layers, the upper one saturated with chlorine, next to this a layer of unchanged chloride, and below this a layer containing a large number of hydroxyl ions. The hydroxyl ions migrate toward the anode, and on coming in contact with an excess of chlorine react in the same way as when a diaphragm is used.

With carbon anodes in the belljar process, a much higher hydrate concentration can be obtained without destroying the middle layer of the neutral solution separating the chlorine from the hydroxide; at the same time, however, the current yield is less than the theoretical. This is due to the fact that free oxygen is always evolved on carbon anodes, producing free hydrochloric acid. The hydrogen ions from this acid migrate toward the cathode and
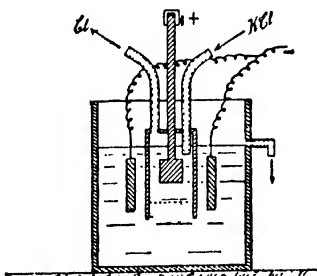
FIG. 81. — THE BELLJAR CELL FOR ELECTROLYZING SODIUM CHLORIDE

[1] Gustav Adolph, Z. f. Elektroch. **7**, 581 (1901).

neutralize the hydroxyl ions migrating toward the anode, and thus prevent their coming in contact with free chlorine. In consequence of this, much more highly concentrated solutions of hydrate can be produced by the belljar process with the same energy yield than by the diaphragm process.[1]

In actual practice the belljar process is always carried out with a circulating electrolyte. Fresh chloride solution flows into the anode compartment, where it must be spread out uniformly over the entire area of the belljar so that the neutral layer will not be disturbed.

In the belljar process the losses of chlorine and hydrate are equal, so that the current yields in chlorine and hydrate must also be equal. The chlorine dissolved in the anode solution is carried through the neutral layer by circulation and is changed to hypochlorite on coming in contact with the hydroxyl ions below. This is reduced on the cathode, producing an equal loss in hydrate. The loss in chlorine at the anode by the evolution of oxygen also produces an equal loss in hydrate, for the hydrochloric acid left behind by the oxygen neutralizes an equivalent amount of hydrate.[2]

With a circulating electrolyte a current yield of from 85 to 94 percent can be obtained, with the concentration of potassium hydrate 120 to 130 g./l., and the chlorine 97 to 100 percent pure, using a current density referred to the area of the belljar of 2 to 4 amp./sq. dm., and from 3.7 to 4.2 volts.[3]

(3) The third method of separating the hydrate from the chlorine consists in depositing the metal in a mercury cathode, which is then removed from the cell and treated with water. The sodium or potassium reacts with the water, forming the hydrate, and the mercury is returned to the cell to be used over again. The losses in this process are due to the recombination of chlorine dissolved in the solution with the alkali metal in the amalgam, and to the reaction of the alkali metal with the water before leaving the electrolyzing cell. The former loss may amount to 100 percent under some circumstances, while the loss due to the decomposition of water is small. In order to reduce the recombination of the chloride and the alkali metal, the current density on the cathode should be high and also the concentration of the amalgam. Strange as it may seem, the potassium amalgam is more resistant to

[1] Adolph, *l.c.*, p. 589.
[2] Otto Steiner, Z. f. Elektroch. **10**, 320 (1904).
[3] Z. f. Elektroch. **10**, 330 (1904).

chlorine, the more concentrated it is. For example, increasing
the concentration of the amalgam from 0.012 percent to 0.06 per-
cent increased the yield in comparable experiments from zero to
90 percent. A current density of 10 amp./sq. dm. gave an 88
percent current yield. Since the principal loss is due to a recom-
bination of the chlorine and the alkali metal, the yield will be the
same for both alkali and chlorine. If the amalgam is covered with
a diaphragm to protect it from the chlorine, current yields of 98
percent can be obtained.[1]

(4) The fourth method of separating the hydrate from the
chlorine consists in using mercury as an intermediate electrode.
The principle of this process is
illustrated in Figure 82. The
electrolytic cell is seen to con-
sist of three compartments; the
two outer are the anode com-
partments containing the graph-
ite anodes AA, and the middle
compartment contains the cath-
ode C, consisting of an iron grid.
The covers of the anode com-
partments have pipes, not shown
in the figure, for leading off the

Fig. 82 — Section of Castner-
Kellner Cell with Intermediate
Mercury Electrode for Elec-
trolyzing Sodium Chloride

chlorine, but the cathode compartment is only loosely covered,
so that the hydrogen escapes in the air.

The partitions separating the compartments do not quite reach
to the bottom of the cell, but the opening is closed by a layer of
mercury covering the bottom of the cell. The alkali metal is
electrolyzed into the mercury in the anode compartment and is
electrolyzed out in the cathode compartment. In the cathode
compartment the amalgam is the anode, and the alkali metal unites
with the hydroxyl ions liberated on it and forms hydrate. In
order to stir up the amalgam so that the alkali metal will get into
the cathode compartment as soon as possible, the whole cell is
slowly tilted back and forth, causing the mercury to flow from one
compartment to the other.

In this system the current density on the cathode must also be
at least 10 amp./sq. dm.[2] The speed of rocking the cell also
affects the yield, an increase in the rapidity decreasing the yield.
One of the difficulties encountered in this process is that if the

[1] F. Glaser, Z. f. Elektroch. **8**, 552 (1902).
[2] Le Blanc and Cantoni, Z. f. Elektroch. **11**, 611 (1905).

alkali metal becomes too dilute in the amalgam, the mercury is itself oxidized in the anode compartment. To avoid this, a part of the current is taken directly from the mercury by a shunted circuit in which there is a suitable resistance to make the shunted current about one tenth of the total current. A decrease in the concentration of the chloride solution reduces the current yield. With a 30 percent potassium chloride solution at a temperature of 40°, and with a current density of 10 amp./sq. dm., Cantoni obtained a current yield in hydrate of 90 percent.

Technical Cells for Hypochlorite, Chlorate, Hydrate, and Chlorine. *Hypochlorite Cells.* — Hypochlorite is produced in less quantity than any of the other products of the electrolysis of sodium chloride. Though it is said that in 1916 the textile industry of Germany used over 175 hypochlorite plants,[1] in this country a solution of bleaching powder is preferred for large-scale work, such as bleaching paper pulp. Hypochlorite is used more for such purposes as disinfecting and deodorizing utensils, drains, and floors in dairies and ice-cream factories, for bleaching in laundries, in knitting and cotton mills, in hospitals for making Dakin's solution, and to a limited extent for other purposes.

Hermite's cell, patented in 1887, was the first cell to be even moderately successful for the electrolytic manufacture of hypochlorite.[2] It consisted of a rectangular box of ceramic with a grooved channel around the top for carrying off the solution of sodium and magnesium chlorides, which entered at the bottom. The cathode consisted of numerous disks of zinc supported on two slowly rotating shafts running through the box and separated from each other by a partition. The anodes, consisting of thin sheets of platinum held on a nonconducting frame, were placed between the zinc disks. In practice this cell gives a current yield of about 40 percent and an energy yield of 2 kilograms of chlorine per kilowatt-day.[3]

An earlier form of cell devised by Kellner had vertical intermediate electrodes consisting of platinum-iridium wire net, wound on glass plates which did not reach to the bottom of the cell. These were held in place by grooves in the sides of the glazed stoneware vessel. The electrolyte circulates through the cell through holes in the bottom and overflows at the top to a vessel

[1] Askenasy, *Technische Elektrochemie*, **2**, 99 (1916).

[2] W. H. Walker, Electroch. Ind. **1**, 440 (1903); Engelhardt, *Hypochlorite und Elektrische Bleiche*, p. 77 (1903).

[3] Engelhardt, *l.c.*

with a cooling coil. The results obtained with this cell are: 10 g. of active chlorine per liter with a current efficiency of 66 percent from a solution containing 10 percent of sodium chloride and a
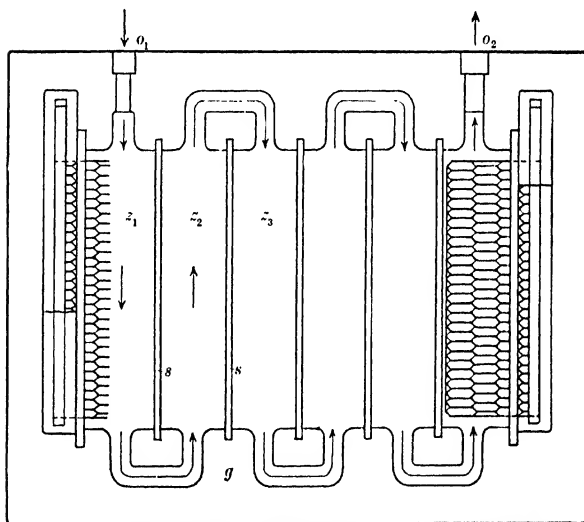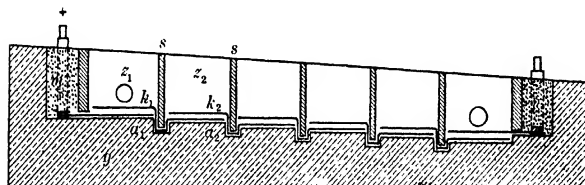
FIG. 83. — SECTIONS OF KELLNER'S HORIZONTAL HYPOCHLORITE CELL

little chromate. The cell takes 5.5 volts, corresponding to 4 kg. of active chlorine per kw.-day while the salt consumption is 10 kg. of sodium chloride per kg. of active chlorine.[1] On account of this poor result, due partly to the current passing to a certain

[1] Foerster, Chem. Ind. **34**, 374 (1911).

extent under the intermediate electrodes in place of through them, and to the circulation which prevents the formation of a diffusion layer at the anode, this cell is no longer used.[1]

Kellner changed the position of the electrodes from vertical to horizontal and to a horizontal circulation of the electrolyte, as shown in Figure 83. This is built by Siemens and Halske.[2] It is a shallow concrete cell divided into compartments by glass partitions cemented in grooves in the sides and bottom. The bottoms of these different compartments are arranged in terraces, so that the electrolyte entering the first compartment will flow as shown by the arrows. The electrolyte enters and leaves each compartment above the electrodes so as not to disturb that in immediate contact with the electrodes. The electrodes are platinum-iridium wire. The cathode of the first cell is connected to the anode of the next under the glass partition marked s. The anodes are about 5 mm. below the cathodes, and the two are separated by glass rods. By this arrangement the hypochlorite is formed in a layer between the electrodes by the meeting of the ascending solution charged with chlorine and the descending hydrate, and there is less opportunity for oxidation at the anode or reduction at the cathode. Calcium chloride and calcium hydrate are also added to prevent reduction, and Turkey red oil to form a diaphragm at the anode to prevent the production of chlorate.

Since this is the most efficient of the hypochlorite cells, its performance [3] is fully described in Table 39.

The latest form of the Schuckert cell made by the Siemens and Halske Company contains 9 or 18 compartments in a stoneware vessel, each compartment containing a platinum anode and two graphite cathodes. Connection is made from the cathode of one compartment to the anode of the next by clamping the platinum sheets A between the graphite plates C as shown in Figure 84, thus forming bi-polar or intermediate electrodes. The walls dividing the cell into compartments are glass so placed that the solution in circulating from one compartment to another must pass in a zigzag direction from top to bottom. Cells are built with

[1] Grube, *Grundzüge der angewandten Elektrochemie*, p. 179 (1922); Foerster, *Elektrochemie wässeriger Lösungen*, p. 697 (1922).

[2] Germ. Pat. 165,486.

[3] Ebert and Nussbaum, Engehardt Monographs, Vol. **38**, *Hypochlorite und elektrische Bleiche*, p. 128 (1910). In calculating the energy 6 volts per cell is assumed.

TABLE 39. THE KELLNER HYPOCHLORITE CELL
WITH HORIZONTAL ELECTRODES

CONC. ACTIVE Cl₄/L. PRODUCED	INITIAL CONC. IN G. NaCl PER L.	REQUIREMENTS FOR 1 KG. ACTIVE CHLORINE	
		Kilowatt-Hours	Kg NaCl
15	100	5.65	6.67
	120	5.46	8.00
	150	5.29	10.00
20	100	6.13	5.00
	120	5.83	6.00
	150	5.56	7.50
25	100	6.72	4.00
	120	6.27	4.80
	150	5.88	6.00
30	100	7.79	3.33
	120	6.98	4.00
	150	6.38	5.00
35	100	10.07	2.86
	120	8.20	3.43
	150	7.14	4.28

or without cooling. If cooling is used, the coils are placed in separate compartments. The concentration of salt used is 100 to 150 g./l. In general the concentration of active chlorine is 18 g./l. This can be obtained with a solution containing 110 g. of sodium chloride per liter and a consumption of 3.2 kw.-days and 6.2 kg. of sodium chloride per kilogram of active chlorine.[1]
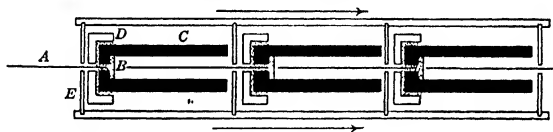
FIG. 84. — PLAN OF SCHUCKERT HYPOCHLORITE CELL

The Haas and Oettel cell, made by Haas and Stahl, in Aue, Germany, has intermediate graphite electrodes lengthened above and below by glass plates. The stoneware cell containing the electrodes is placed in a vessel also filled with brine. Each compartment in the electrolyzer has a hole in the bottom, so that when the current is flowing the evolution of hydrogen causes the liquid between the electrodes to rise and overflow to the outside vessel while liquid

[1] Foerster, *Elektrochemie wasseriger Lösungen*, p. 702 (1922).

enters the electrolyzer through the openings in the bottom. The outer vessel contains cooling coils.[1] With a solution containing 150 g./l. of sodium chloride and fresh electrodes 10 to 12 g. of active chlorine per liter can be made with a yield of 3.4 to 3.6 kg. of active chlorine per kilowatt-day, and a consumption of 14 kg. of sodium chloride.[2]

The Electro Chemical Company of Dayton, Ohio, makes two types of hypochlorite cells:
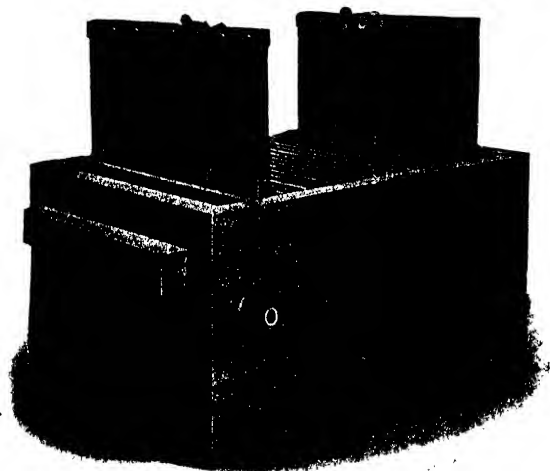
Fig. 85. — Hypochlorite Cell; The Electro Chemical Company

(1) Those in which brine enters at the inlet compartment, flows up and down over intermediate graphite electrodes, and passes out as finished hypochlorite. One of these cells is shown in Figure 85. It is made of soapstone and is $25\frac{3}{4}$ in. long, 18 in. wide, and $11\frac{1}{4}$ in. high. The intermediate electrodes are held in grooves cut in the walls, and are made of glass and carbon as shown in Figure 86. Brine containing 50 lb. of sodium chloride per 100 gal. of water (60 g. of sodium chloride per liter of water) passes at the rate of 50 gal./hr. The current is 70 amp. at 110 volts. The solution

[1] Germ. Pat. 130,245. Billiter, *Die electrochemischen Verfahren der chemischen Gross-Industrie*, **2**, 363 (1911).
[2] Kirchner, Wochenblatt f. Papierfabrikation, 1906, p. 2248.
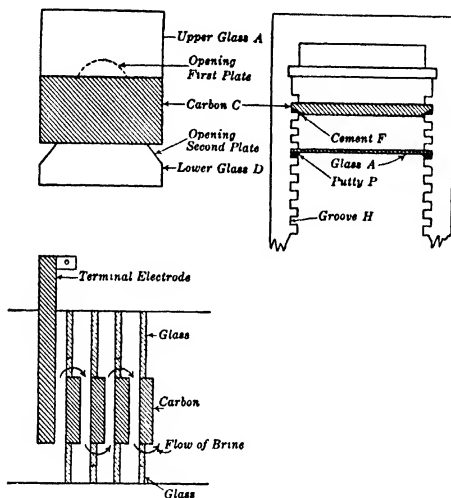
FIG. 86. — SHOWING CONSTRUCTION OF CELL IN FIG. 85

leaving the cell contains 6 to 7 g. of active chlorine/l. and has a temperature of 43° C. The energy yield is 3.1 kg./kw.-day (3.5 lb./kw.-hr.). Cells of very similar construction are made for use with only circulation within the cell. In this case there is a space between the bottom of the electrodes and the floor of the cell so the cell can be drained.

(2) The other type of cell is placed in a storage tank and circulation takes place between the storage tank and the electrolyzer, as shown in Figures 87 and 88. Either intermediate graphite electrodes are used, or in some forms the electrodes are connected in multiple, giving a low-voltage cell (4.6 volts). The latest form contains graphite anodes and metal-grid cathodes, which give better efficiency than graphite. The largest size contains 100 gal. and takes 3000 amp. With a solution containing 50 lb. of sodium chloride per 100 gal. of water (60 g./l. of water) this cell produces a concentration of 15.2 g./l. of active chlorine with a yield of 3.51 kg./kw.-day (3.10 kw.-hr./lb.) when cooled to 27° C.[1]

[1] Data on these cells were kindly furnished by Mr. E. E. Niswonger, president of the company.

Chlorate Cells. — As shown above, chlorate is made in a neutral or slightly alkaline solution with not more than $66\frac{2}{3}$ percent current efficiency, while if the solution is slightly acid the current efficiency may be 90 percent. In this country it is customary to use neutral solutions, as the process requires less attention than the acid process. In the French Alps acid solutions containing chromate are said to be used.[1]

FIG. 87. — LOW VOLTAGE HYPOCHLORITE CELL; THE ELECTRO CHEMICAL COMPANY

When platinum was not so expensive, it was used as anodes for chlorate at a current density of 10 to 20 amp./sq. dm., but at present prices graphite anodes and iron cathodes are employed. In most cases the platinum has been sold and graphite substituted. A 25 percent potassium chloride solution is electrolyzed at 70° to 75° C. until nearly saturated with chlorate, when it is drawn off and allowed to cool, with crystallization of the chlorate. The frequency with which cells have to be emptied can be regulated by the current concentration. It is evident that if a large volume of electrolyte is electrolyzed with a small number of electrodes, it will not become saturated as soon as if more electrodes and more current are used. The less frequently the cells have to be drained, the less the labor cost per pound of chlorate will be.

FIG. 88. — SHOWING CIRCULATION IN CELL SHOWN IN FIG. 87

The temperature is also determined by the current concentration. If a low current concentration is desired to save labor cost, it might be necessary to supply heat in addition to that of the current. The cell temperature would also depend on the heat conductance of the walls of the cells. In designing a cell these details would have to be deter-

[1] Foerster, *Elektrochemie wasseriger Lösungen*, p. 705 (1922).

mined by experiment. The cell may consist of any material not attacked by chloride or chlorate, such as concrete or iron.

Perchlorate Cells. — No descriptions of perchlorate cells are to be found in the literature, but they are doubtless as simple as chlorate cells. Platinum or platinum-iridium anodes must be used. They are also cooled to prevent the temperature rising above 50° or 60° C. As shown above a good current efficiency is obtained at this temperature by increasing the current density sufficiently. To cool to room temperature would be expensive and is probably never done.

Technical Cells for Alkali Hydrate and Chlorine. — *Diaphragm Cells.* — Among the methods separating chlorine and hydrate produced in the electrolysis of alkali chlorides, a porous diaphragm is the most extensively used. The main difficulties with diaphragms are that they get stopped up and have to be cleaned or replaced from time to time, and they do not give complete separation of the products of electrolysis because they do not prevent electrolytic migration; hydroxyl ions migrate into the anode compartment and produce chlorate. Only pure chloride is used. Calcium and magnesium are precipitated as carbonate, and sulfate by barium chloride. Iron and alumina must also be absent. Many different ways have been devised of using diaphragms, as will be seen by the descriptions of the following cells.

The oldest diaphragm cell is that developed by the Griesheim-Elektron Chemical Company. Its present form dates from 1892,[1] and it is still used to a large extent abroad, for electrolyzing both sodium and potassium chlorides. This cell consists of an iron vessel E (Figure 89) heat insulated by infusorial earth, I. It is 4.8 m. long, 3.3 m. wide, and 1 m. deep (15.7 by 10.8 by 3.3 ft.), and contains about 4.8 cb. m. of solution (1270 gal.), excluding the anode solution and the volume of the heating pipes. This tank contains 12 anode compartments consisting of Portland cement diaphragms made on an iron frame according to the method of German patent No. 34,888. This method consists in mixing cement with a solution of sodium chloride and hydrochloric acid, and allowing to harden six weeks, after which they are soaked in water for 4 to 6 weeks to dissolve the salt, leaving a porous diaphragm. The anode compartments inclosed by these diaphragms are 1.1 m. long, 0.75 m. wide, and 1 m. high (3.6 by 2.5 by 3.3 ft.). Each has a cement lid in which 6 carbon (or a larger number of magnetite) anodes A are held, as well as the perforated vessel

[1] Askenasy, *Einführung in die technische Elektrochemie,* **2,** 180 (1916).
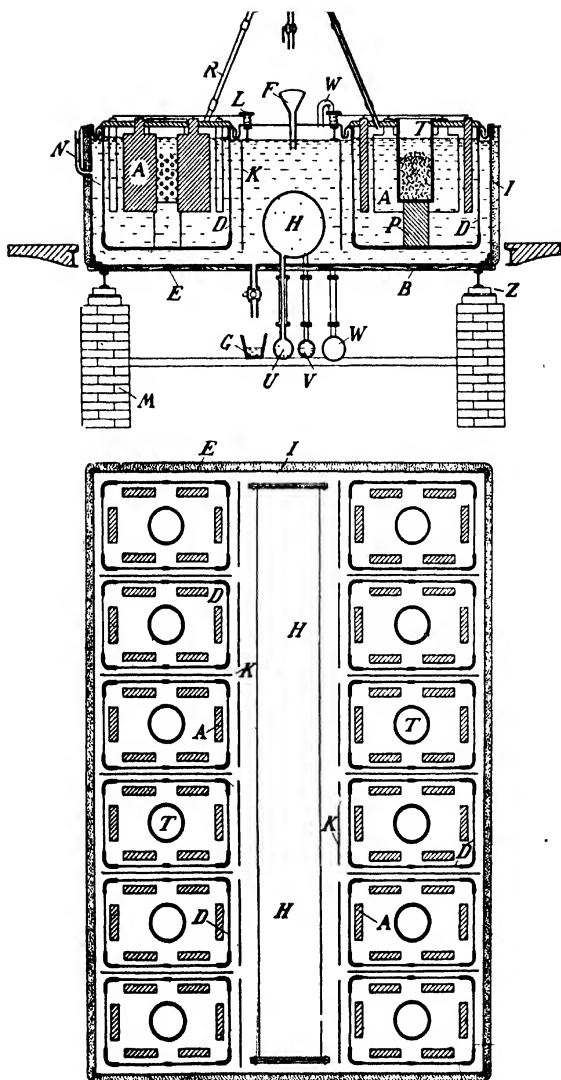
FIG. 89. — SECTIONS OF GRIESHEIM-ELEKTRON ALKALI-CHLORINE CELL

T for containing solid chloride. The iron sheets K and the containing vessel itself act as cathodes. The cathode compartment is also covered with a lid containing an exit pipe for hydrogen and a funnel F for filling with chloride solution. H is a heating pipe through which exhaust steam is passed. All anodes of the 12 anode compartments are connected in parallel. The temperature is 80° C., the anode current density 2 amp./sq. dm. and the total current 2500 amp. at 3.6 volts. Magnetite anodes require 0.4 volt more. The cathode compartment contains initially 2.7-n chloride and electrolysis continues until the alkalinity is 1.1 to 1.2-n, when it is drawn off. The current efficiency is 80 to 84 percent.

In cells such as the one just described hydroxyl ions migrate into the anode compartment and cause a loss in hydrate and chlorine. This can be prevented by causing the electrolyte to flow through the diaphragm toward the cathode, and a number of cells have been devised in which this is done. The characteristic feature of all of these cells is that the cathode is not immersed in the electrolyte, but is only wetted by what percolates through
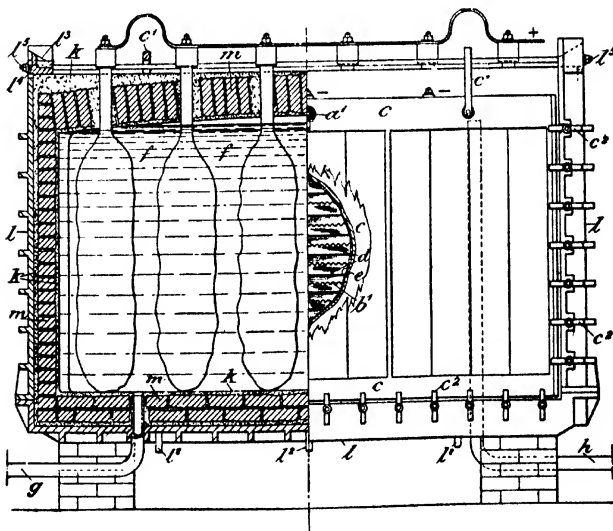
FIG. 90. — SECTION OF HARGREAVES-BIRD ALKALI-CHLORINE CELL

the diaphragm. One of the earliest of these cells is the Hargreaves-Bird cell.

This consists of a cast-iron box 10 feet in length, 14 inches in width, and 5 feet in height.[1] It is divided into three compartments by two cement-asbestos diaphragms made on heavy copper gauze, which forms the cathode. The space between the diaphragms is the anode compartment, through which brine circulates. There is no liquid in the cathode compartment except what percolates through the diaphragm. Steam and carbonic gas are blown through the two outer compartments and change the hydrate formed on the outside of the diaphragm to sodium carbonate. This cell takes 2000 amperes at from 4 to 4.5 volts. The anode is a row of gas carbons, which last 30 to 40 days. The diaphragms last about the same length of time.

The Hargreaves-Bird cell is shown in Figure 90, which is a partial longitudinal section and side elevation, and in Figure 91, which is a section perpendicular to the length.[2] The outside frame l is of iron lined with cement and bricks m, which are saturated with tar to prevent leakage. The space f is the anode compartment through which the chloride solution circulates, entering through the pipe g and leaving through h. The diaphragms may be made of asbestos paper, the pores of which have been filled with hydrated silicate of lime or magnesia.[3] In the cathode chamber a number of copper strips b are placed, imbedded in cement e, extending from the cover plate c to the cathode d, and inclined downward. These direct the condensed vapor against the cathode to wash away the alkali as it is formed. The lower edges of the strips have openings, in order to allow the steam and gas to pass freely over the cathode. a', a' are the injectors for supplying carbonic acid gas and steam to the cathode chambers. l^2, l^2 are pipes for draining the cathode chambers. The chlorine passes from the anode chambers to the towers, where it is absorbed by milk of lime.

The West Virginia Pulp and Paper Company, Mechanicsville, New York, use this cell for making their bleaching solutions.[4] This plant consists of two rows of 14 cells each, all connected in series. At 85° C. this cell gives a solution containing 15 percent

[1] L. Rostosky, Z. f. Elektroch. **11**, 21 (1905); Electrochem. and Met. Ind. **3**, 350 (1905).
[2] U. S. Pat. 655,343 (1900).
[3] U. S. Pat. 596,157 (1897).
[4] Electrochem. and Met. Ind **6**, 227 (1908).

sodium carbonate and 97 to 98 percent
chlorine with a current efficiency of 92
percent at a current density of 2.8
amp./sq. dm. and 4.2 volts per cell.

The Townsend cell is represented in
cross section in Figure 92, and in per-
spective in Figure 93.[1] The anode space
is inclosed between a lid C, two vertical
diaphragms D, and a non-conducting
body H. Graphite anodes pass through
the lid on the cell. The perforated iron
cathode plates S are in close contact
with the diaphragms. These plates are
fastened to two iron sides I, which form
the cathode compartment. The anode
compartment is filled with brine T, and
the cathode compartment with kerosene

oil K. The
brine percolates
through the
diaphragm,
and, when the
current is

FIG. 2.

FIG. 91 — SECTION OF HAR-
GREAVES-BIRD ALKALI-
CHLORINE CELL

turned on, it contains hydrate. The
aqueous solution, on passing the dia-
phragm, comes in contact with the kero-
sene and forms drops which fall to the
bottom of the compartment, are collected
in the pocket A, and are drained off
through P. The electrolyte is in this
way removed from the cathode sooner
than if allowed to flow down the cathode
as in the Hargreaves-Bird cell. The so-
lution leaving P contains 150 grams of
sodium hydrate and 213 grams of salt
per liter. The salt is separated by evap-
oration and is used over again. The
percolation is from 15 to 30 liters an
hour for a 2500-ampere cell and counter-
acts diffusion nearly completely.[2]

FIG. 92. — SECTION OF
TOWNSEND ALKALI-CHLO-
RINE CELL

[1] Electrochem. and Met. Ind. **5**, 209 (1907).
[2] Baekeland, Electrochem. and Met. Ind. **7**, 314 (1909).

The Townsend cell is 8 feet in length, 3 feet in depth, and 1 foot in width, and consists of a U-shaped concrete body against which the two iron side plates are clamped. A rubber gasket is placed between the concrete and the iron to make a tight joint. Brine circulates through the anode compartment, and during its passage the specific gravity falls from 1.2 to 1.18. On leaving the cell it is resaturated and is then ready to be passed through again. There is a loss in kerosene which amounts in cost to about two dollars a day for a large plant.

FIG. 93. — TOWNSEND ALKALI-CHLORINE CELL

The diaphragms of the Townsend cell consist of a woven sheet of asbestos cloth, the pores of which are filled with a mixture of iron oxide, asbestos fiber, and colloid iron hydroxide. This mixture is applied with a brush like ordinary paint. Diaphragms may be renovated by scrubbing and washing the surface with water, allowing to dry, and repainting with this mixture. This operation is not necessary more than once in five weeks, and sometimes not for several months.

The current efficiency of the Townsend cell is as high as 96 or 97 percent under ordinary conditions, with a current density on the anode of 15.5 amp./sq. dm. (144 amp./sq. ft.) and about 4 volts on each cell.[1] This cell has been in use at Niagara Falls in the plant of the Development and Funding Company since 1906. This plant originally consumed 1000 kilowatts, and according to latest accounts it was being increased to four times this capacity.

[1] For laboratory tests on the efficiency of this cell, see Richardson and Patterson, Trans. Am. Electrochem. Soc. 17, 311 (1910).

FIG. 94. — ALLEN-MOORE ALKALI-CHLORINE CELL

The chlorine produced contains 2 percent carbon dioxide. The more recent Townsend cells are said to be built for 5000 amp.[1]

The Allen-Moore cell[2] also has vertical diaphragms, through which the electrolyte percolates to an iron cathode supporting the diaphragm. It was first installed in Wilmington, Del., in 1912. As shown in Figure 94 it consists of a rectangular frame of reënforced concrete, formed by a base, ends, and a chamber at the top. The diaphragms and perforated iron cathodes are clamped against this frame closing the openings in the sides. The space between the diaphragms is the anode compartment. Graphite anodes pass through the top of the cell and are about $\frac{1}{2}$ inch from the diaphragms. These are made of asbestos and last 3 months. Recently in pulp and paper mills paper pulp has been used for diaphragms. These are $\frac{1}{4}$ inch thick and last about ten days. Brine is admitted to the anode compartment through a hard rubber float valve which controls its level in the anode compartment, passes through the diaphragm, and is partly charged into hydrate at the cathode. This solution, containing 12 percent salt and 8 to 10 percent caustic soda, flows into the channel trough of the steel frame cathode box.

The following average values were found in long tests at different plants :

Current, 1344 amp., voltage 3.55, current efficiency 95 percent, energy efficiency, assuming the decomposition voltage of sodium chloride is 2.3 volts, 61.7 percent.

The chlorine is entirely free from hydrogen, and contains only air and small amounts of carbon dioxide. The current can be increased to 1900 amp. at 4.5 volts, with 91 percent current efficiency.

This cell is now made in the following sizes :

	1000 AMPERE	1500 AMPERE	2000 AMPERE
Length	5 ft. $5\frac{1}{2}$ in.	5 ft. $6\frac{1}{2}$ in.	8 ft. 1 in.
Width	13 in.	14 in.	14 in.
Height	$38\frac{1}{2}$ in.	$44\frac{1}{2}$ in.	$44\frac{1}{2}$ in.
Approximate weight of cell set up ready for operation	1000 lb.	1200 lb.	1800 lb.

The Marsh cell[3] is similar to the Allen-Moore cell as regards the way the diaphragms are placed. Its chief feature is the close-

[1] Foerster, *Elektrochemie wässeriger Lösungen*, p. 740 (1922).

[2] Mitchell, Chem. Met. Eng. **21**, 370 (1919). This cell is made by the Electron Chemical Company, Portland, Me.

[3] C. W. Marsh, Tr. Am. Electroch. Soc. **39**, 507 (1921); U. S. Pat. 1,302,824 (1919).

ness with which the anode and cathode are brought together for saving power and floor space, as shown in Figure 95. The anodes consist of graphite rods 4.4 cm. in diameter (1.75 in.) and 60 cm. long (24 in.) placed horizontally one above the other with spaces between and pinned to a rectangular piece of graphite which conducts the current to the rods and acts as a support. These anodes last two years. The cathode consists of perforated sheet steel corrugated horizontally to conform to the graphite rods. Asbestos paper diaphragms are laid on the cathodes conforming
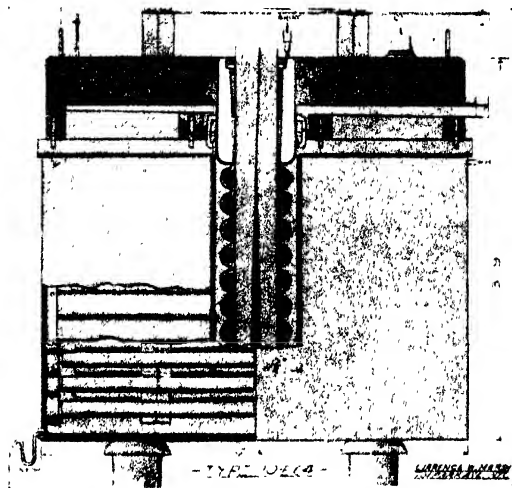
FIG. 95. — MARSH ALKALI-CHLORINE CELL

to the corrugations. They last six months. These cells are built in different sizes to take from 50 to 5000 amp. at 3.8 volts. The current efficiency is 90 percent and the energy efficiency from 65 to 73 percent. These cells are all 13 in. wide and $3\frac{2}{3}$ ft. high with variable lengths according to the capacity desired. A 625-ampere cell is 2 ft. 7 in. long, a 3750-ampere cell is 12 ft. 10 in. long.

The Nelson cell,[1] Figure 96, consists of a rectangular steel tank made of $\frac{1}{4}$-inch steel plate, in which is mounted a U-shaped

[1] Carrier, Tr. Am. Electroch. Soc. **35**, 239 (1919); The Warner Chemical Company, New York.

cathode plate of perforated sheet steel closed at the ends by blocks of cement mortar. The inner part of this cathode plate is lined with an asbestos diaphragm and forms the anode compartment of the cell. Steam is blown through the space between the cathode sheet and the outer containing tank. An inverted rectangular box of slate slabs closes the top of the anode compartment and supports the anodes consisting of graphite blocks, the dimensions of which are 10 by 10 by 43 cm. (4 by 4 by 17 in.). These are screwed on to graphite rods 6 cm. in diameter (2.5 in.) and 30 cm. long (12 in.). There is an automatic feeding device consisting of a float which presses a dull knife edge against the rubber tubing through which the brine is supplied to the cell. The diaphragms
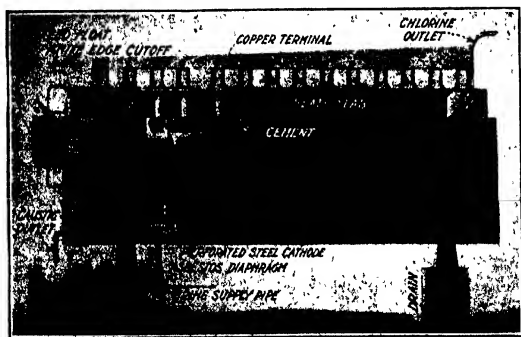
Fig. 96. — Nelson Alkali-Chlorine Cell

are renewed every 6 to 8 months. It is said to require more labor to change diaphragms in this cell than in the Allen-Moore cell, but Nelson cells require less floor space. Nelson cells are built for 1000 amp. After reaching normal working conditions the cathode liquor contains 10 to 12 percent of sodium hydrate and 14 to 16 percent of sodium chloride. The guaranteed ampere efficiency is 86 percent, but 90 percent is generally reached. The average voltage is 3.7 volts, corresponding to an energy efficiency of 56 percent based on 90 percent current efficiency and 2.3 volts as the decomposition voltage of sodium chloride. The floor space required is one square foot for 2.5 lb. of chlorine per day (12.5 kg./sq. m.). The chlorine averages 99 percent pure.

The Gibbs cell,[1] shown in Figure 97, has a cylindrical vertical

[1] Kershaw, Chem. Met. Eng. **24**, 81 (1921).

diaphragm. The cathode which surrounds the diaphragm has a number of inward projections imbedded in the diaphragm for reducing its resistance. The cathode compartment is filled with liquid. The diaphragm and cathode are shown at 8 and 9. The asbestos diaphragm is thicker at the bottom, in order to make the
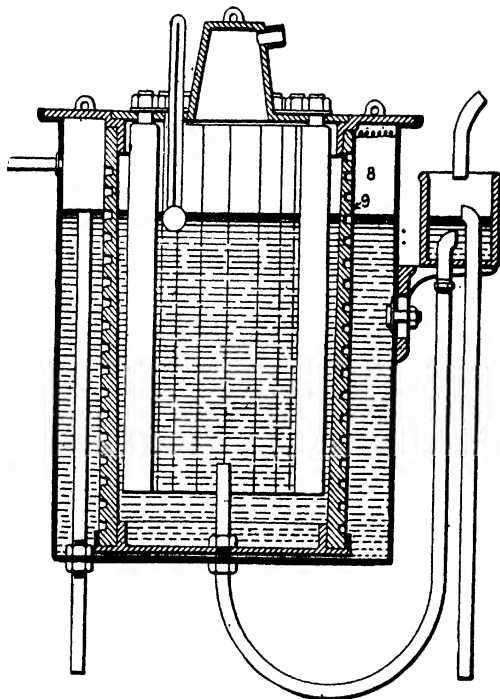
FIG. 97. — SECTION OF GIBBS ALKALI-CHLORINE CELL

rate of percolation the same at the top and bottom. The cathode jacket is of sheet steel. The projections of the cathode plate which are the principal feature of this cell may be obtained by punching holes in the sheet and then pressing the sheet around the diaphragm with the rough edges on the inside, or the sheet may be corrugated longitudinally. These points are said to remove

the caustic soda from the action of the current, and reduce the loss due to the discharge of hydroxyl ions. It is also said that the permeability of this diaphragm is maintained for a longer time than one placed on a cathode without projections.

There is an iron lid in which the anodes are fixed, and a separate annular ring holding the cathodes and diaphragm. Data on this cell have not been published. It is used by the Pennsylvania Salt Manufacturing Company at Wyandotte, Michigan.
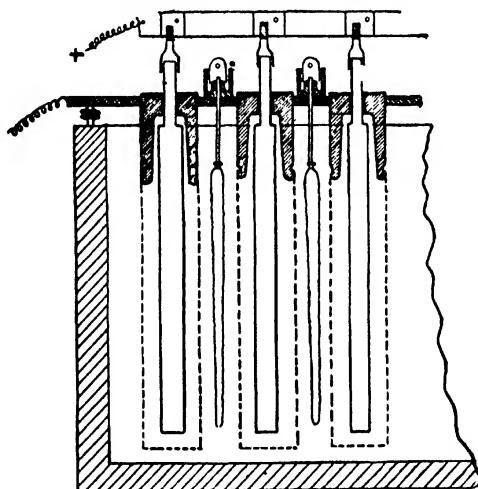
Fig. 98. — Anodes and Cathodes of the Basel Alkali-Chlorine Cell

The cell made by the Société pour l'Industrie Chimique à Bâle is employed in a number of works in France, Italy, and Switzerland.[1]

The peculiarity of this cell is its so-called "propulsive" cathode, which reduces the floor space required for a given output and also gives a fairly high percentage of alkali. The cathode is placed in a narrow-meshed asbestos bag having the same form as the cathode. The hydrogen liberated in this narrow cathode chamber rises to the surface, where a froth is produced consisting of bubbles of hydrogen contained in shells consisting of the solution of alkali carried up by the hydrogen. This froth overflows into a chamber

[1] Kershaw, Chem. Met. Eng. **24**, 169 (1921); Brit. Pat. 11,872 (1913).

where the hydrogen is separated from the cathode liquid. The part of the cathode bag extending above the electrolyte is impermeable to hydrogen. Two of these cathodes are shown in Figure 98, which shows only the bags and iron tubes through which the froth rises, but the cathodes inside the bags are not indicated. The electrolyte is sucked through the diaphragm by the continual removal of froth, and this counterbalances the migration of hydroxyl ions. Carbon anodes are fixed in nonconducting, long, narrow, belljars. The anodes are also surrounded by asbestos diaphragms shown as dotted lines in the figure. These cells are 40 in. deep and 5 ft. by 10 ft. in area. The concentration of the alkali is 11 to 13 percent sodium hydrate or 15 to 17 percent potassium hydrate; the sodium chloride content is not given. The chlorine has less than 2 percent carbon dioxide. Due to suppression of the migration of hydroxyl ions, the anodes last three years. The cathodes and bags are cleaned every six to eight months of the layer of lime which stops up the pores. The current efficiency is not given.

The diaphragms so far described are all vertical, but diaphragms may also be placed in a horizontal position. The advantages of the vertical position are principally mechanical, such as smaller floor space required, ease in changing diaphragms, a more convenient shape of anodes, and the settling of impurities to the bottom of the tank and not on the diaphragms, which would increase their resistance. On the other hand, horizontal diaphragms are better from an electrochemical standpoint because the rate of percolation is the same over the whole surface, while in the vertical position the percolation is greater at the bottom than at the top. Furthermore, any hydroxide that migrates back into the anode compartment lies on the surface of the diaphragm and is not mixed with chlorine, as this does not stir up the solution around the cathode in the horizontal position.

Cells with horizontal diaphragms have been made by Le Sueur,[1] by Carmichael,[2] and by Billiter.[3] Only the Billiter cell will be described. It is shown in Figure 99.[4] The cell walls B of concrete are placed on an iron tray E. T is a diaphragm of pure asbestos cloth fastened to the cell walls with cement, and is supported by

[1] Z. Elektroch. 1, 140 (1894); 4, 215 (1897); 5, 29 (1898); J. Am. Ch. Soc. 20, 868 (1898).
[2] Z. Elektroch. 1, 213 (1894).
[3] Billiter, Z. Elektroch. 23, 333 (1917).
[4] Askenasy, Technische Elektrochemie, 2, 216 (1916).

an iron-wire cathode K with wires 3 to 4 mm. in diameter which rests on supports and is electrically connected to the iron tray. A mud D of some material resistant to the action of alkali and chlorine, such as barium sulfate, is placed on the asbestos cloth so the liquid will not pass through too rapidly. In order to get the proper size of grain the sulfate is precipitated from a hot
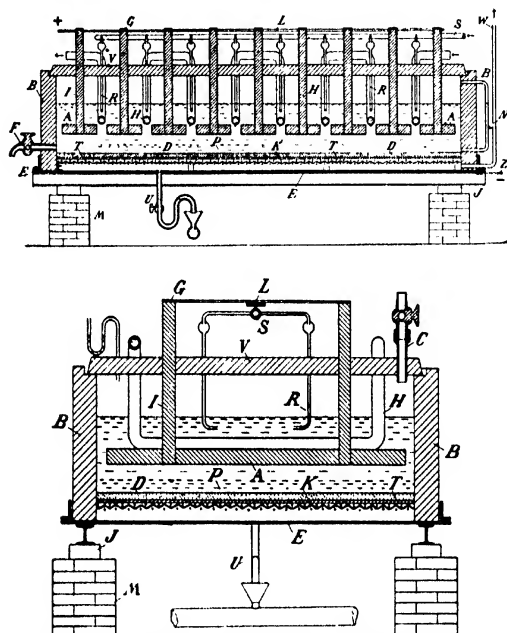
FIG. 99. — SECTIONS OF BILLITER HORIZONTAL DIA-PHRAGM ALKALI-CHLORINE CELL.

solution. About $\frac{1}{50}$ of its weight of asbestos fiber is mixed with it in order to make it firmer. H is a heating pipe. The anodes are graphite plates, perforated or curved to allow the escape of chlorine. The solution in contact with the cathode becomes charged with alkali and drops into the empty space below the cathode. At the working temperature of 85° to 90° C. this cell produces a solution containing 12 to 16 percent of sodium hydrate,

or 18 to 20 percent of potassium hydrate, with a current efficiency
of 95 percent. With 4.6 amp./sq. dm. at the anode 3.5 volts
are required per cell. A cell takes from 2000 to 3000 amp. The
chlorine contains traces of oxygen and 1.5 percent of carbon
dioxide.

The electrolyte is fed to the anode compartment through a
number of tubes R. The level of the liquid is shown by N. These
cells are in use at a number of plants in Germany and at Niagara
Falls by the Niagara Alkali Company.[1]

The belljar process is carried out by the Oesterreichischer Verein
für chemische und
metallurgische
Produktion in
Aussig, and at
several places in
Germany. Fig-
ure 100 shows
two cross sec-
tions of the cell,
25 of which are
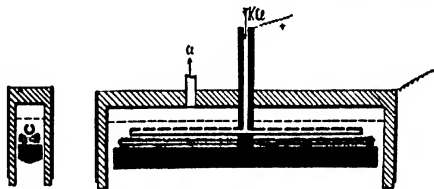
FIG. 100 — SECTIONS OF BELLJAR ALKALI-CHLORINE
CELL

placed side by side in each bath.[2] Each cell takes 23 amp.
The solution leaving the bath is said to contain 100 to 150 grams
of alkali hydrate per liter, at a current yield of 85 to 90 percent
and with 4 to 4.5 volts per cell.[3]

Billiter has modified the belljar process so that only one large
belljar per cell is necessary, in place of the large number in the
Aussig process.[4] As shown in Figures 101 and 102, the cathodes
are placed immediately under the anodes, and the hydrogen is
conducted away by the asbestos tubes which surround the cathode.
These tubes are not intended to confine the hydrate ; it passes
through easily. There is evidently a uniform current density and
a uniform flow of liquid throughout the cross section of this belljar,
and the electrodes are closer together. The voltage is less than in
the Aussig cell. The cells are made of reënforced concrete, and
have the following internal dimensions : 5.5 m. long, 1.1 m. wide,
and 1.3 m. high (18 ft. by 3.6 ft. by 4.3 ft.). There are three
cement lids, each carrying eight anodes, whose dimensions are:
100 cm. by 18 cm. by 5 cm. (39 by 7 by 2 in.). The current den-

[1] Allmand, Met. Chem. Eng. 11, 20 (1913).
[2] Z. f. Elektroch. 7, 925 (1901).
[3] Haeussermann, Dinglers polyt. J. 315, 475 (1900).
[4] Met. Chem. Eng. 11, 20 (1913).

sity when running at 85° C. is 4 to 6 amp./sq. dm.; by changing other conditions this can be increased to 14 amp./sq. dm. The T-shaped cathodes are iron. Saturated, unpurified brine is used. The cathode liquor produced contains 12 to 13 percent of sodium hydrate and 20 percent sodium chloride, with the flow at the rate 350 l. per day. The final product contains 97 percent of sodium hydrate, 1.2 percent of sodium carbonate, and 1.8 percent of sodium chloride. At room temperature these cells take about 4 volts, at 85° C. 3.1 volts. The current efficiency is about 92 percent
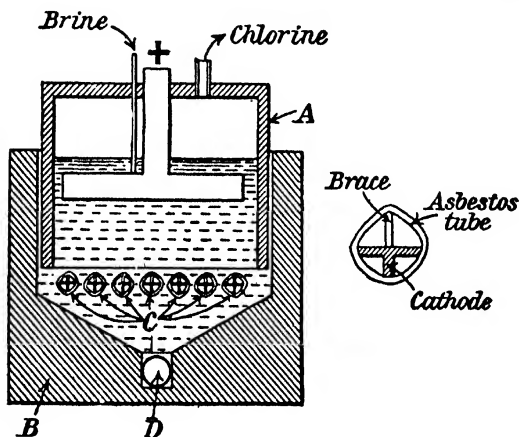
FIG. 101 — SECTION OF BILLITER-LEYKAM ALKALI-CHLORINE CELL

for 3-n to 4-n alkali (12 to 16 percent). The principal advantages of this cell are: freedom from diaphragm troubles, the use of impure brine, low attendance charges, and low energy consumption.

Mercury Cells. — The following are the principal advantages of cells with mercury cathodes or with intermediate electrodes: [1]

(1) Production of more highly concentrated alkali, up to 40 percent with a saving in evaporation,

(2) the alkali has no sodium chloride,

(3) the hypochlorite concentration can be kept very low, so that the anodes are very little attacked and there is scarcely any carbon dioxide in the chlorine, but it does contain hydrogen. It is no longer true that the current efficiency in mercury cells is

[1] Taussig, in Askenasy's *Technische Elektrochemie*, **2**, 101 (1916).

better than that in diaphragm cells, due to improvements in the diaphragm cells, while the voltage required in mercury cells is higher.   The current efficiency of mercury cells is not 100 percent, due to the formation of hydrogen either by deposition or by subsequent action of the electrolyte on the amalgam.
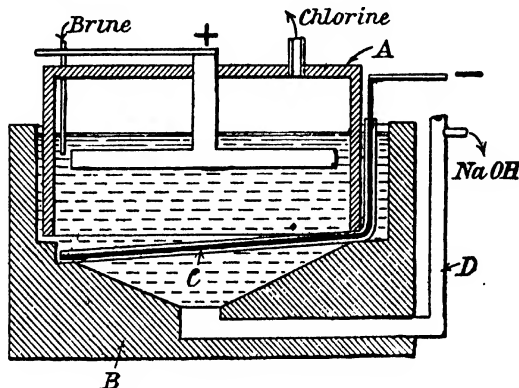
FIG. 102. — SECTION OF BILLITER-LEYKAM ALKALI-CHLORINE CELL

A simple form of mercury cell is that of Solvay and Company.[1] Two cells are connected together so that the amalgam formed in the electrolysis cell is decomposed in the other by contact with water. The electrolyzing cell shown in Figure 103 consists of long, narrow,
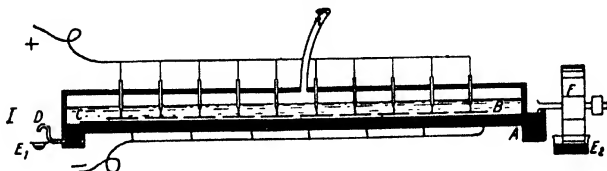
FIG. 103. — SECTION OF SOLVAY ALKALI-CHLORINE CELL

iron trays lined with cement and slightly tilted. · Mercury flows continuously from B to C, and the electrolyte flows in the same direction.   It enters at 30° C. and leaves at 60° C.   At C the upper layer richest in sodium flows over the partition and to the de-

[1] Germ. Pat. 104,900 (1898); Z. Elektroch. **7**, 923 (1901); Tr . Faraday Soc. **5**, 258 (1910).

composing cell, where a stream of water flows in the opposite direction to that of the amalgam and acts on it chemically. The alkali from the decomposing chamber is 35 to 37 percent of sodium hydrate. The anodes are platinum.

The cells take 10,000 to 15,000 amp. at 5 volts, and 12 to 15 amp./sq. dm. The advantages of these cells are their simplicity and the large units.

In the Castner cell mercury forms an intermediate electrode. It [1] is represented in Figure 82. It is a slate box 4 feet square and 6 inches deep, the joints of which are made tight with rubber cement.[2] Two partitions, reaching to within $\frac{1}{16}$ inch of the bottom, divide the cell into three compartments. The two outside compartments contain the graphite anodes A, and the middle compartment the iron cathode C. Brine circulates through the anode compartments, and pure water is supplied to the cathode compartment. The cell is pivoted on two points at one end and the other is raised and lowered about $\frac{1}{2}$ inch once a minute, causing the mercury to circulate between the anode and cathode compartments. The hydrate leaving the cathode compartment contains about 24 percent of sodium hydrate (sp. gr. 1.27). This is evaporated to solid hydrate in large iron pans. Each cell takes about 100 pounds of mercury, which is a very large item of expense. The current for each cell is 630 amperes at 4.3 volts, and the current efficiency is about 90 percent. The current density on the mercury is 12 amp./sq. dm.; on the anodes, 16 amp./sq. dm.

On account of the loss in sodium in the amalgam by chemical reaction with the solution, there is not sufficient sodium in the amalgam to carry all of the current from the amalgam to the solution, and the current would oxidize some mercury, if it all passed from the mercury surface to the solution. This is avoided by conducting 10 percent of the current from the mercury by an external conductor to the cathode.

It was formerly thought that the decomposition voltage of sodium chloride between graphite and iron, which is 2.2 volts, would not be changed by inserting an intermediate mercury electrode, but that the excess voltage required for decomposition on the mercury cathode would be balanced by the action of sodium in the amalgam in the other compartment. It does not act this way, however, because of the low concentration of sodium in the amal-

[1] U. S. Pat. 528,322 (1894).

[2] J. W. Richards, Electrochem. Ind. **1**, 12 (1902); Le Blanc and Cantoni, Z. Elek. **11**, 609 (1905).

gam. It even takes 0.2 volt more to send the current from the amalgam to the iron cathode.[1]

The Whiting cell,[2] shown in Figures 104, 105, and 106, is a massive concrete structure supported on four concrete pedestals, from which it is insulated. It consists of a shallow box divided into two compartments, A and B, by a concrete partition. The bottom of the decomposing chamber is divided by low glass par-
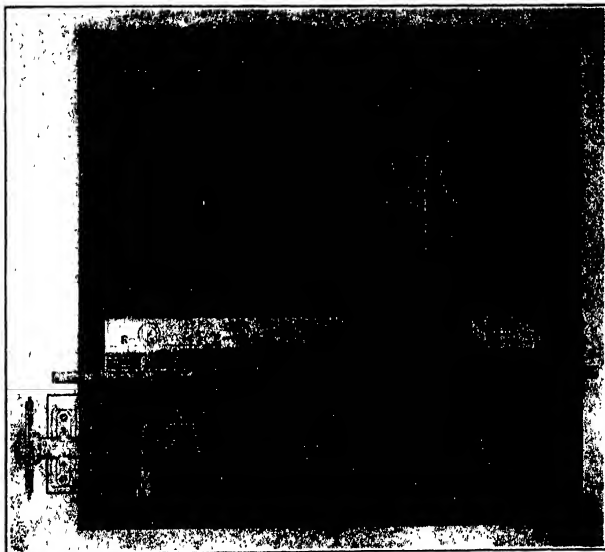
Fig 104. — Horizontal Section of Whiting Alkali-Chlorine Cell

titions into a number of sections having V-shaped bottoms sloping at a slight angle toward the central slot D. These slots lead through the concrete partition into the oxidizing chamber B, where they turn upward and are closed by valves E. The valves are operated by the cams F, which are attached to a slowly revolving shaft G. The other ends of the slots are connected by the channel H, called the distributing level. This connects with a

[1] From experiments by Mejdell, Foerster, *Elektrochemie wässeiriger Lösungen*, p. 771 (1922).
[2] Jasper Whiting, Trans. Am. Electrochem. Soc. 17, 327 (1910).

secondary channel I, which leads through one of the side walls of the cell to a pump J, at the extreme end of the oxidizing compartment. Mercury covers the bottom of the decomposing compartment, filling the above-described sections to a common level. The anodes K are slabs of Acheson graphite, perforated to allow the chlorine to escape, and rest upon the ledges L, placed at the ends of the section in such a way as to make a very short distance
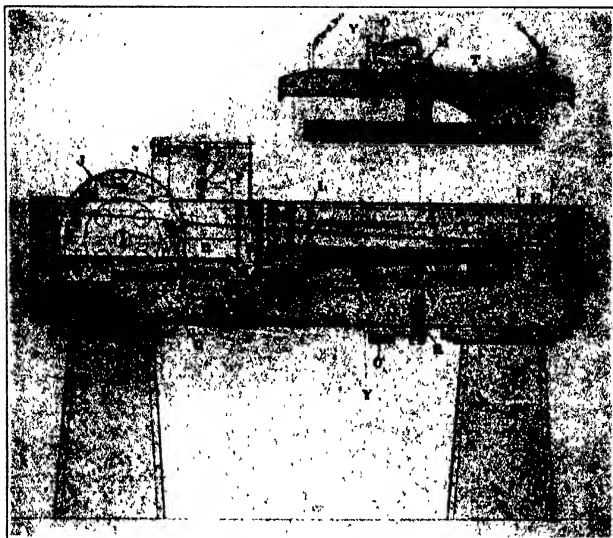
Fig. 105. — Vertical Section of Whiting Alkali-Chlorine Cell

between the anode and the mercury cathode. The anodes are connected to the dynamo by the leads M.

The oxidizing chamber is divided into three compartments P, lined with graphite and sloping downward in successively opposite directions, forming a zigzag path to the pump pit Q, where the stoneware rotary pump J is placed. Brine fills the decomposing chamber, and water or alkali hydrate fills the oxidizing chamber.

The action is as follows: The floor of several sections of the decomposing chamber is covered with mercury, maintained at a common level by the distributing level. The current flows

from the anode through the brine to the mercury and out by the
iron rods R, partly imbedded in the concrete.   When the elec-
trolysis has proceeded about two minutes, the valve at the point
of exit of one of the sections is opened by the action of the cam,
and the entire mass of sodium amalgam in the section sinks into
the slot and through the connecting pipe into the oxidizing cham-
ber.   When the mercury is out of the cell, the valve is closed by
the cam.   Mercury free from sodium then flows into the empty
chamber by way of the distributing level, until the common level
is reached.   In the meantime the sodium amalgam in the oxidizing
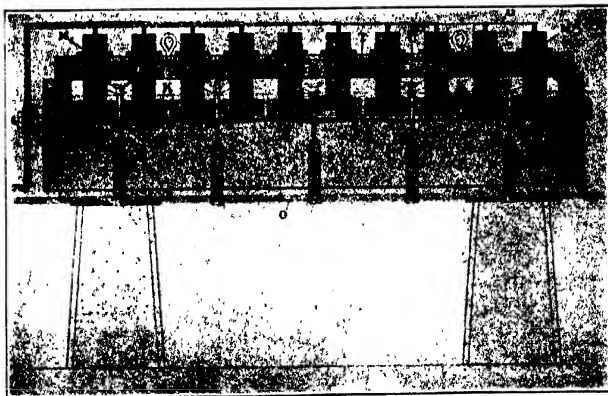
Fig. 106. — Vertical Section of Whiting Alkali-Chlorine Cell

chamber flows by gravity over the graphite plates P to the pump
pit.   On reaching this point the mercury has been deprived of its
sodium, and is raised by the pump into the wall pipe of the
decomposing chamber, completing the cycle.

The brine is fed in between the electrodes from the receptacles
S, equal in number to the sections of the decomposing chamber.
They are formed in the cover of the decomposing compartment,
and are connected by a channel T.   Glass tubes lead from the
bottom of the receptacle S through the anode and terminate
below the surface of the mercury near the middle of each section.
As long as the sections are filled with mercury the lower ends of the
tubes are sealed, but when the mercury is drawn off, a definite
quantity of concentrated brine flows into the section.

The graphite slabs in the oxidizing chamber contain a large number of channels through which the mercury flows. The sides of the channels extend into the caustic solution and form the cathode of a short-circuited couple. It is difficult to maintain good contact between the graphite and mercury on account of the hydrogen evolved, but this difficulty was overcome by boring holes ½ inch deep and ⅛ inch in diameter at frequent intervals in the channels, and filling them with pure mercury at the start. This mercury remains pure and makes good contact with the amalgam and the graphite.

The cell used at the Oxford Paper Company's works in Rumford, Maine, is 1.8 meter square. It consists of five sections and takes a current of from 1200 to 1400 amperes at 4 volts. This corresponds to an anode current density of 11 amp./sq. dm. The current efficiency is from 90 to 95 percent. The temperature is about 40 degrees. Each cell requires from 350 to 375 pounds of mercury. A 20 percent hydrate solution is obtained, though one with 49 percent can be made if desired. The chlorine gas is 98 percent pure, the remaining 2 percent being hydrogen.

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CHAPTER XIII

THE PRODUCTION OF HYDROGEN AND OXYGEN BY THE ELECTROLYSIS OF WATER

HYDROGEN and oxygen have a number of technical applications that require their manufacture on a large scale. Such uses are welding with the oxyhydrogen flame, as is done in joining the lead plates of storage batteries, the hydrogenation of oils, for reducing purposes, such as tungstic acid to metallic tungsten, and for filling balloons. Oxygen is used for chemical and medicinal purposes.

Hydrogen and oxygen are produced on a large scale by the electrolysis of water, though other methods are also employed. The chief points to be considered in different types of electrolyzers are (1) the purity of the gases, (2) the energy efficiency, (3) the durability of the materials of which the cell is constructed, and (4) the simplicity of construction. Some of the principal cells are the following. A solution of sodium hydrate is used in all.

The Electrolabs Company of Pittsburgh makes cells in four sizes:

AMPERES	HOURLY PRODUCTION, CUBIC FEET AT ROOM TEMPERATURE		GUARANTEED EFFICIENCY, CUBIC FEET PER KW.-HR AT ROOM TEMPERATURE	
	Oxygen	Hydrogen	Oxygen	Hydrogen
250	2	4	3.75	7.5
600	4.8	9.6	3.75	7.5
1000	8	16	3.9	7.8
5000	40	80	3.5	7.0

The smallest of these cells is represented in Figure 107 and the inside parts in Figure 108. Each cell has three narrow compartments, the middle containing two cobalt-plated cathodes each and the two outer each a cobalt-plated anode. Pure asbestos diaphragms are held in sheet-metal frames; two in each cell. The electrodes are independent of the casing.

The cell made by the Burdett Manufacturing Company of Chicago is shown in Figure 109. It is a cell placed in an open steel

tank of electrolyte. This inner cell is open at the bottom and contains the electrodes. The electrodes are connected in multiple and are separated by asbestos diaphragms. Each cell takes 400 amp. and produces 76.8 cu. ft. of oxygen and 153.6 cu. ft. of
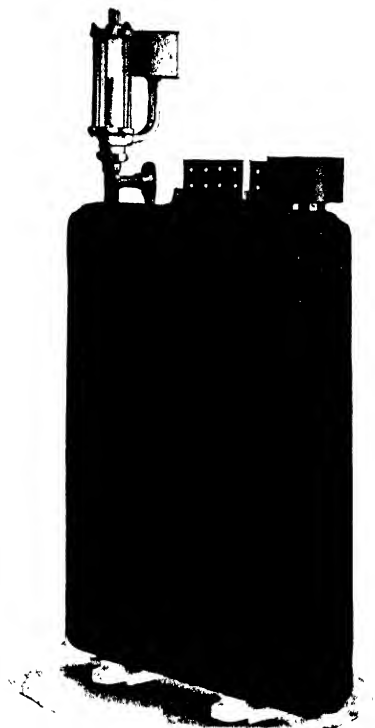
Fig. 107. — Electrolabs Company's Electrolytic Hydrogen-Oxygen Generator

hydrogen per day, at 20° C. Each cell requires 1.95 volts. The surface of the electrolyte between the walls of the two cells is covered with oil to prevent the absorption of carbon dioxide from the air.

Oxygen Compartment   Asbestos Diaphragm   Hydrogen Compartment
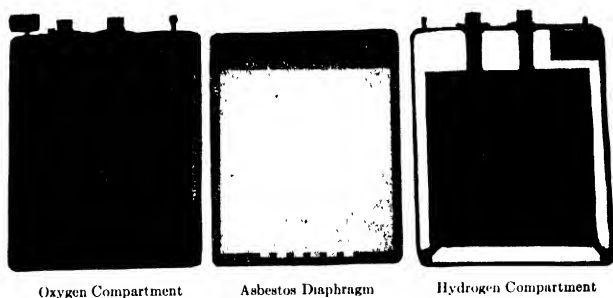
FIG. 108. — INSIDE PARTS OF GENERATOR SHOWN IN FIG. 107

The cell shown in Figure 110 is made by the International Oxygen Company of Newark, New Jersey.   A group of these is assembled like a filter-press.   Bipolar electrodes are used, which are separated by asbestos diaphragms placed between the electrodes. These have rubber edges to prevent the leakage of the electrolyte, and are the weakest point of these cells, as the rubber is attacked by the hydrate and requires replacement from time to time.   The anode is nickel plated because nickel has a low overvoltage for oxygen and because it is not attacked as an anode in alkali hydrate. This generator may be operated at currents up to 1000 amp.   The oxygen is not less than 99.5 percent pure and the hydrogen not less than 99.75 percent.

The Toronto Railway Company has recently brought out a cell designed by Wm. G. Allen,[1] but a full description of this cell is not yet available.   It will therefore be discussed very briefly.   This cell has bipolar electrodes, insulated from the pressed sheet steel casings, and separated from each other by asbestos cloth diaphragms.   Six cells are assembled into units by bolting them together.   The electrolyte circulates through the cells, both leaving and entering at the top.   The outside dimensions are 40 inches high by 24 inches wide.   A unit of six cells takes up 3 square feet of floor space, corresponding to 3.37 square inches of floor space per cubic foot of hydrogen per hour.   The cells take 1350 amperes, corresponding to 432 amp./sq. ft. of projected electrode area.   A further advantage is the small weight of electrolyte required, and the small weight of the cell itself.

[1] Tr. Am. Electroch. Soc. **41**, 239 (1922).   Cost calculations are also given.
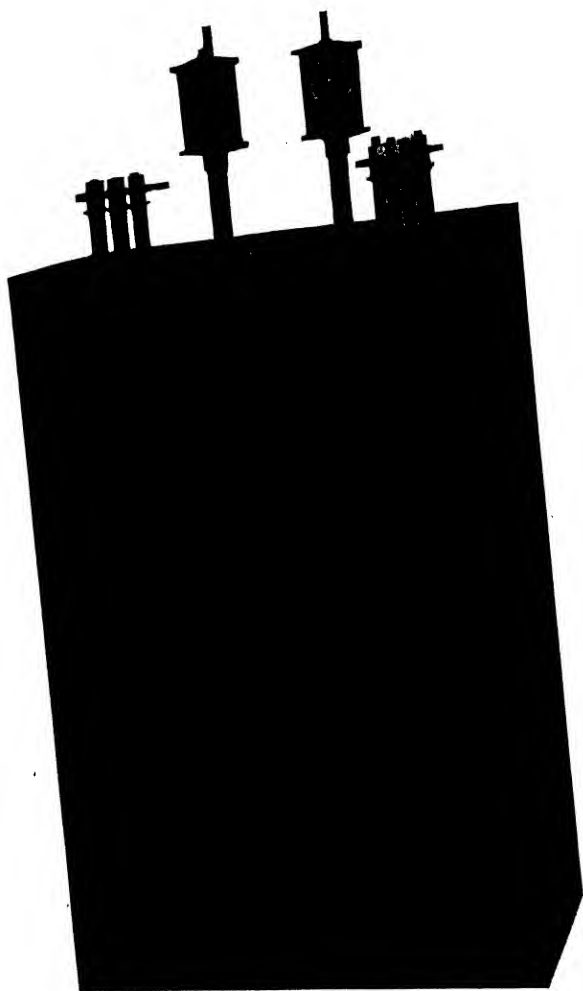
FIG. 109. — BURDETT MANUFACTURING COMPANY'S ELECTROLYTIC HYDROGEN-OXYGEN GENERATOR

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OXYGEN OFFTAKE WATER FEED HYDROGEN OFFTAKE

BELL JARS

GAS TRAP

GAS TRAP

OVERFLOW PIPE

FRONT END OF GENERATOR

ELECTROLYTE INLET

INSPECTION DOORS

ELECTROLYTE RESERVOIR

NORMAL LEVEL OF SOLUTION WHEN IN OPERATION

CONTACT SURFACE

OXYGEN GAS CHAMBER HYDROGEN GAS CHAMBER

ANODE FRAME

ANODE PLATE NICKEL PLATED

CONTACT SURFACE

ASBESTOS DIAPHRAGM

CATHODE PLATE
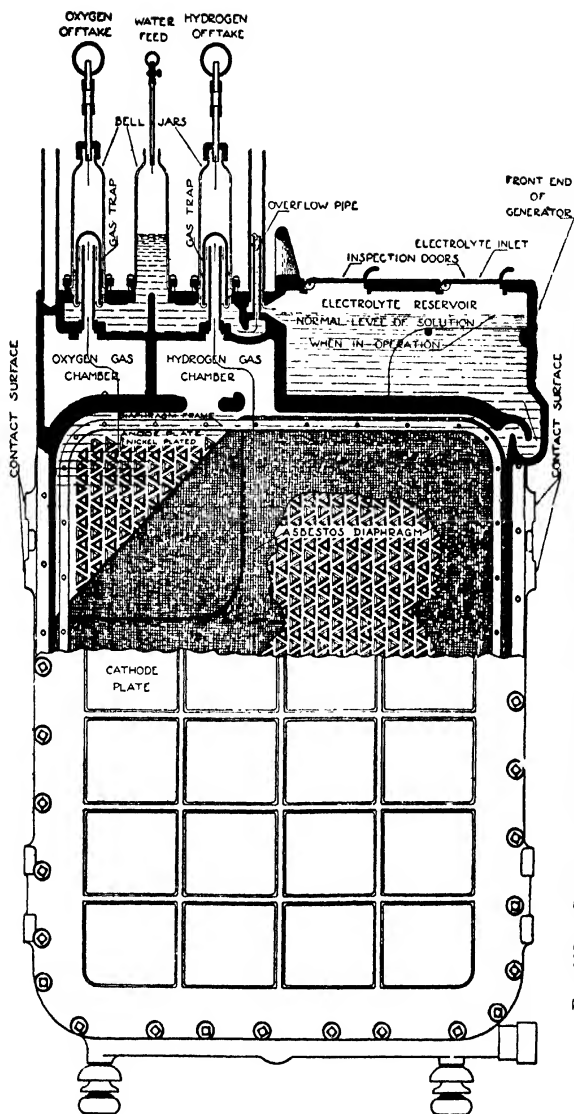
Fig. 110. — Section of International Oxygen Company's Electrolytic Hydrogen-Oxygen Generator

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CHAPTER XIV

PRIMARY CELLS

A PRIMARY cell is one so arranged that the energy of a chemical reaction is obtained as an electric current, and in which the chemicals are not regenerated by passing the current through the cell in the opposite direction. When the cell is run down, fresh chemicals must be supplied. A secondary cell, or accumulator, is one in which chemicals are regenerated by passing through the cell, after discharge, a reverse current from some other source. A battery is a group of cells.

Before the invention of dynamos, primary batteries were the main source of electric energy; but since this method of generating electricity is too expensive for use where a large quantity of energy is needed, they were employed only for very light work and for experimental purposes. They are still used extensively for electric bells, for ignition, railroad signals, and similar purposes. Primary cells of special forms are also the standards of electromotive force, for which see Part I.

The first primary cell was due to Volta, and consisted in a negative pole of zinc and a positive pole of copper dipping into a solution of salt or dilute acid. The electromotive force of this cell rapidly falls off if an appreciable current is taken from it, on account of the hydrogen liberated on the positive pole. This develops a back electromotive force and also increases the resistance of the cell itself. The cell is then said to be polarized. In order to have an efficient cell, polarization must be avoided. In the Smee cell, this was done by substituting platinized silver for the positive pole in place of the copper in the Volta cell. The rough surface caused the bubbles of hydrogen to escape more rapidly.

In the Grove cell, devised in 1831,[1] the cathode consisted of platinum dipping into nitric acid contained in a porous cup. Outside the cup was dilute sulfuric acid and a zinc negative pole. In this case the nitric acid acts as a depolarizer, oxidizing the

[1] For an account of primary cells, see Wiedemann, *Die Lehre von der Elektricität*, 1, 243 (1893).

hydrogen to water and itself being reduced to nitrous gases.   The electromotive force of this cell is between 1.6 and 1.7 volts.

The Bunsen cell is a Grove cell with carbon in place of platinum for the positive pole.

In the chromic acid cell, due to Poggendorff, the electrolyte is a solution of sulfuric acid and potassium or sodium bichromate, containing about 8 parts of potassium bichromate, 16 of concentrated acid, and 100 of water.   The positive pole is carbon and the negative zinc, which is withdrawn from the liquid when not in use.   The chromic acid acts as depolarizer.   The reaction is:

$$3 \, Zn + Cr_2O_7^{--} + 14 \, H^+ = 2 \, Cr^{+++} + 3 \, Zn^{++} + 7 \, H_2O.$$
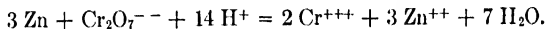
The electromotive force is about 1.3 volts.

Problem. — Write the separate equations at the two electrodes that add up to this equation.

In the Daniell cell, brought out in 1836, the positive pole is copper dipping in a concentrated solution of copper sulfate, and the negative is zinc dipping in sulfuric acid.   Copper is deposited on the positive in place of hydrogen, thus avoiding polarization, and zinc goes in solution, forming zinc sulfate.   The electromotive force of this cell is about 1.1 volts.

The gravity cell is a form of the Daniell cell patented by Varley in 1854, but which did not become generally known until 1884. It was at one time the principal commercial form of the Daniell cell.   The gravity cell derives its name from the way in which the two solutions are prevented from mixing.   At the bottom of a glass jar is a horizontal copper electrode covered with copper sulfate crystals and a saturated solution of copper sulfate.   On this solution is carefully poured a dilute sulfuric acid solution, in which a horizontal zinc electrode is immersed.   When in use the migration of the copper ions toward the cathode prevents their reaching the zinc, while if the cell stands on open circuit, the copper sulfate would finally reach the zinc by diffusion and cover it with a layer of copper.   This cell should therefore always be kept on a closed circuit through a few ohms resistance.

These cells have at present little more than historical interest. The use of primary cells is now nearly entirely confined to the Leclanché and the Lalande cells.   Leclanché cells, in the form of dry cells, are used for light work, the Lalande type, for heavy work. Leclanché brought out his cell in 1868.   It consists of a zinc rod forming the negative pole and dipping into a solution of ammonium

chloride. The positive pole is carbon in contact with manganese dioxide for a depolarizer. When the circuit is closed, zinc goes in solution as zinc chloride and the ammonium radical is deposited on the carbon, which breaks up into ammonia and hydrogen. The ammonia dissolves and the hydrogen is oxidized by the manganese dioxide to water. It is also allowable to consider that the cathode reaction is the reduction of quadrivalent to trivalent manganese in the saturated solution of manganese dioxide :

$$MnO_2 + 2 H_2O = Mn^{4+} + 4 OH^-,$$
$$Mn^{4+} = Mn^{3+} + F,$$
$$Mn^{3+} + 3 OH^- = \tfrac{1}{2} Mn_2O_3 + \tfrac{3}{2} H_2O.$$
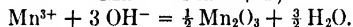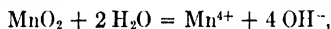
· The total result is: $MnO_2 + \tfrac{1}{2} H_2O = \tfrac{1}{2} Mn_2O_3 + OH^- + F.$

The depolarizing action of the mixture of dioxide and carbon is dependent on the relative sizes of the two materials.[1] This depolarization is not rapid, however, consequently not much current can be taken from a Leclanché cell at a time without the voltage dropping considerably, but it recovers on standing. The electromotive force of this cell on open circuit differs from one cell to another, varying from 1.05 to 1.8 volts. In a recent form of Leclanché cell oxygen of the air is used in place of manganese dioxide.[2]

The hydroxyl ions produced at the cathode form undissociated NH_4OH with the NH_4^+ ions, and the equilibrium $NH_4^+ + OH^- = NH_4OH = NH_3 + H_2O$ is established. Some of the ammonia escapes, but the greater part enters into the equilibrium : $ZnCl_2 + 2 NH_3 = Zn(NH_3)_2Cl_2$; this salt frequently crystallizes from the solution. Zinc hydroxide may be also formed by the action of air and water on zinc and form an insulating layer over the surface of the zinc electrode.

Dry cells are Leclanché cells with only a small amount of moisture, and are much more generally used than those containing a large amount of solution. In 1919 over 79 million dry cells of the larger sizes were manufactured in the United States, and over 94 million flashlight cells.[3] Zinc acts as the container and negative pole of the cell. This is covered with cardboard for insulation. The electrolyte is an aqueous solution of ammonium chloride, with zinc chloride added to reduce local action, held in an absorbent

[1] Thompson and Crocker, Tr. Am. Electroch. Soc. **27**, 155 (1915).

[2] Fery, Brass World, **18**, 24 (1922); C. r. **172**, 317 (1921).

[3] Circular of the Bureau of Standards, No. 79, *Electrical Characteristics and Testing of Dry Cells*, p. 5 (1923).

material lining the zinc container and in the mixture of carbon and manganese dioxide. The electrolyte is also sometimes made into a jelly with some colloidal material, such as gum traganth, agar-agar, gelatin, flour, or starch. The zinc is usually not amalgamated in American cells, but amalgamation is more common in European cells. The positive pole is a carbon rod imbedded in the mixture of carbon and dioxide.

Pyrolusite, a hydrated manganese dioxide, is the ore used almost exclusively for manufacturing dry cells. Unhydrated ores, such as polianite, are not suitable. The ore must be free from nickel, copper, and cobalt, but one percent of iron is not unusual, and three percent is allowable in some cases. For small dry cells artificially prepared dioxide is sometimes used, but the shelf life of these cells is reduced. An average composition of this filling mixture is the following: [1]

> 10 parts of manganese dioxide,
> 10 parts of carbon or graphite, or both,
> 2 parts of ammonium chloride,
> 1 part of zinc chloride.

Sufficient water is added to give a proper amount of electrolyte to the cell, depending on the original dryness of the materials, their fineness, the quality of the paper lining, and similar factors. The usual specifications for the manganese dioxide are that it shall contain 85 percent of the dioxide, usually refined ore, and less than 1 percent of iron. The cell is sealed up on top with a pitch composition to hold in the filling material and to prevent the cell from drying. The carbon rod extends above the seal and is provided with a binding screw. European cells usually are provided with a vent for the escape of gases, but American cells are generally completely sealed over the top. The gases can escape through the porous carbon electrode.

The electromotive force of this cell is between 1.5 and 1.6 volts. On a short circuit through an ammeter, a cell will give from 18 to 25 amperes. The energy output of a cell of the usual dimensions, 15 cm. high and 6.25 cm. in diameter, discharged to 0.2 volt continuously, varies from about 20 watt-hours when discharged through 2 ohms to 57 watt-hours when discharged through 40 ohms.[2] Of course the smaller the current the more complete

[1] Burgess and Hambuechen, Tr. Am. Electrochem. Soc. 16, 97 (1909).
[2] Ordway, Tr. Am. Electroch. Soc. 17, 341 (1909).

the depolarization. When the external resistance is 64 ohms or more, depolarization is complete.

The two principal forms of dry cells are (1) the paper-lined cells and (2) the bag-type cells. In the paper-lined cells shown in Figure 111 the zinc container is lined with pulpboard consisting of sulfite fiber and ground wood. The manganese dioxide mixture is then tamped in around the carbon rod, and the pulpboard lining is folded down over the top. This method of construction is common in America, but is unusual in European cells.

In the bag-type cells the manganese dioxide mixture is contained in a cloth bag, as shown in Figure 112. The carbon rod and mixture is wrapped in muslin and tied with a string. Some kind of spacer, such as heavy Manila cord, is desirable, and the

Fig. 111. — Paper-lined Dry Cell

Fig. 112. — Bag-type Dry Cell

space between the bag and the container is filled with the electrolyte thickened with flour or some other gelatinous material. These cells do not give as high a current when short-circuited, as the paper lined. This is the test usually employed in this country for dry cells.

Dry cells deteriorate on standing before using, and in order to avoid this, desiccated cells are made up without water, and are filled with water several hours before putting into service. Other cells are only partially assembled, and are quickly assembled when needed.

Another form of dry cell is 25 cm. (10 in.) high by 12.5 cm. (5 in.) in diameter and weighs 4.5 kg. (19 lb.) These have a steel in place of a zinc electrode. The open-circuit voltage is 0.9 volt and the short-circuit current is only 4 to 6 amp. They are intended for closed-circuit at not more than 0.05 amp. or intermittent work with larger currents.

The Lalande cell was brought out in 1883, and is manufactured by Thomas A. Edison, Inc., at Bloomfield, N. J., under the name of the Edison-Lalande cell. This cell, shown in Figure 113, consists of a copper oxide plate between two zinc plates dipping in a 20 or 25 percent solution of sodium hydroxide. In the larger sizes the cell contains two copper oxide and three zinc plates. The containing jar is heat-resisting glass. The zinc plates have mercury added to them during casting, so that they are amalgamated throughout. The copper oxide plates are made from copper scale, which is finely ground and then roasted until thoroughly oxidized. The oxidized powder is then mixed with a new and improved binder and is pressed into cakes a little larger than desired in the finished product. These cakes are then dried and baked at a bright red temperature, which decomposes the binder entirely and leaves the plate in a porous state. This new binder is the chief improvement in recent years in the manufacture of these cells.[1] After cooling, the plates are reduced to copper at the surface by zinc dust, to make them conduct. They are then washed and are ready for use. The hydroxide solution is covered with a heavy mineral oil to prevent its creeping up the zinc plates and corroding them. Discharge curves are shown in Figure 114. The capacity varies from 200 to 1000 ampere-hours, depending on the size of the battery. In the latest form of this cell the positive and negative plates are assembled in a unit rigidly fastened together which the user attaches to the cover of the cell.

The zinc plates are now cast with rectangular depressions near the bottom edge for showing when the cell is nearly used up. These " indicator pannels " are carefully calibrated so that they become eaten out before the main body of the plate is sufficiently corroded to alter its shape and prevent the cell from functioning

FIG 113. — THE EDISON-LALANDE PRIMARY CELL

[1] Private communication from Mr. I. S. Dunham, Chief Engineer.

properly. These pannels are easily inspected without removing from the glass container.

The primary cells described above are comparatively unimportant compared with one which is not yet realized, but on which a great deal of time and work has been spent. This is the cell in which carbon and oxygen are the elements consumed. The present method of producing work by the combustion of coal to run steam engines is very inefficient, as only about 15 percent of this energy is obtained as work, the rest being lost as heat. If it were possible to devise a cell in which carbon and oxygen would unite with the production of an electric current and no other form of energy, at ordinary temperature, a much greater amount of energy could be obtained.

In order to calculate [1] the free energy, or energy that is obtainable as useful work, of the reaction in question,

$$C + O_2 = CO_2,$$
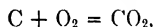
consider a reaction chamber, as shown in Figure 115, containing carbon, oxygen, carbon monoxide, and carbon dioxide in equilibrium at a given temperature. The chamber has two pistons separated from it by semipermeable membranes. The semipermeable membrane at the end of the cylinder containing oxygen is permeable to oxygen only, and that at the end of the cylinder containing carbon dioxide is permeable only to carbon dioxide. The maximum work that this reaction can produce is then obtained by the following reversible process : one mol of oxygen is admitted to the oxygen cylinder at atmospheric pressure
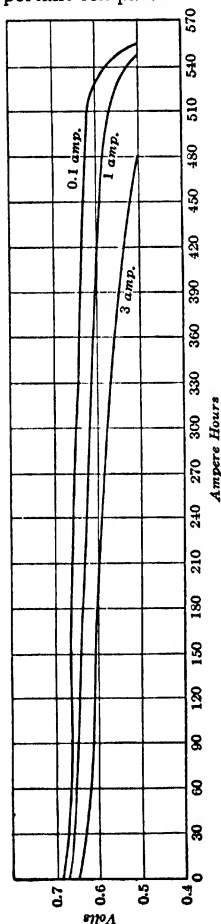
FIG. 114. — DISCHARGE CURVES OF EDISON-LALANDE PRIMARY CELL

[1] Nernst, *Theoretische Chemie*, 8–109 d., p. 781 (1921).
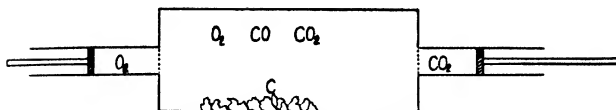
FIG. 115. — REACTION CHAMBER

and is allowed to expand reversibly to the equilibrium pressure of oxygen p_{O_2} in the reaction chamber. The work produced is

$$W_1 = RT \log \frac{1}{p_{O_2}}.$$

The oxygen is then forced into the reaction chamber through the semipermeable membrane. In order to preserve equilibrium, one mol of carbon dioxide must be simultaneously withdrawn at the equilibrium pressure p_{CO_2} into the carbon dioxide cylinder. The work produced in these two steps is evidently zero. The carbon dioxide must then be compressed to atmospheric pressure, in which step the work produced is

$$W_2 = RT \log \frac{p_{CO_2}}{1}.$$

The sum of W_1 and W_2 is the maximum work obtainable:

$$W_1 + W_2 = RT \log \frac{p_{CO_2}}{p_{O_2}}. \tag{1}$$

It would be impossible to measure the pressure of oxygen in this mixture directly, but its value at 1000° C. can be obtained as follows: It has been found experimentally that at 1000° C. carbon dioxide dissociates to 0.06 percent, according to the reaction:

$$2\,CO_2 \rightleftarrows O_2 + 2\,CO.$$
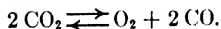
At a total pressure of one atmosphere, the equilibrium pressures for this system are then:

Carbon dioxide . . . . 0.9991 atmosphere
Carbon monoxide . . . . . 0.0006 atmosphere
Oxygen . . . . 0.0003 atmosphere

Substituting in the equation for the mass action law,

$$K(p_{CO_2})^2 = p_{O_2}(p_{CO})^2, \tag{2}$$

$$K(1)^2 = (0.0003)(0.0006)^2. \tag{3}$$

It has also been found that at 1000° C. and atmospheric pressure an equilibrium mixture of carbon monoxide and dioxide in the presence of carbon has the following pressures:

Carbon monoxide . . . . 0.993 atmosphere
Carbon dioxide . . . . . 0.007 atmosphere

Since K is known from equation (3), the pressure of oxygen in this system can be computed by substituting in equation (2):

$$K(0.007)^2 = x(0.993)^2.$$

From this, $x = 5.4 \times 10^{-15}$ atmosphere.

Substituting in equation (1),

$$W_1 + W_2 = 1273 \, R \log \frac{0.007}{5.4 \times 10^{-15}}$$
$$= 70,600 \text{ calories at } 1000° \text{ C.}$$

This gives the free energy of the reaction at 1000° C., and it may be found at room temperature as follows: The heat of the reaction at room temperature is $Q = 97,650$ calories, and it would be approximately the same at the absolute zero, on account of the small change in the heat capacity of carbon and oxygen before and after uniting. This would also be the free energy at the absolute zero, since free energy and the total energy of a reaction are equal at this temperature. The free energy at the absolute temperatures 1273° and 0° being known, it may be interpolated for 20° by the formula,

$$W_1 + W_2 = 97,650 - \frac{97,650 - 70,600}{1273} \times 293$$
$$= 91,470 \text{ calories at } 20° \text{ C.}$$

The ratio of the free to the total energy is therefore approximately $\frac{9\frac{1}{4}}{9\frac{3}{4}}$, corresponding to 94 percent.

If the carbon of the carbon electrode enters the electrolyte as an ion with four positive charges, and the oxygen as an ion with two negative charges, the electromotive force of this cell would be found from the equation,

$$4 \, \mathbf{EF} = 91,000 \text{ calories};$$

from which $\mathbf{E} = \dfrac{91,000}{4 \times 23,100} = 0.99$ volt.

The difficulties in realizing this cell consist in finding an electrolyte in which carbon will dissolve, and in making an oxygen

electrode.   So far they have been insuperable, and at present there seems very little prospect of success.

Problem. — From the heat of the reaction $CO + 1/2 \, O_2 = CO_2$ + 68,000 cal. at 25° C. and the data given above, calculate the relation between free and total energies at 25° C. for this reaction and the electromotive force of the cell.   *Ans.* Free energy = 0.87 of total energy; $E = 1.3$ volts.

Attention has been called by Ostwald [1] to an important point in this cell, that the carbon and oxygen must form the opposite poles of the cell and must act on each other through an intervening electrolyte.   If the carbon and oxygen acted directly on each other, local action would result, and no current would be produced.

A number of attempts have been made to make a carbon oxygen cell, all of which employed some fused salt or hydrate as electrolyte.   This is a disadvantage to start with, for energy will be lost by radiation in keeping the cells at a temperature of several hundred degrees centigrade.   One of the first of these attempts was made by Becquerel [2] in 1855.   In this cell the carbon was dipped into melted potassium nitrate, and the positive electrode was platinum.   This cell could never be successful, for the carbon is brought directly in contact with the oxidizing substance.   Also, the oxygen was not taken directly from the air, but was in the expensive form of a nitrate.

In 1896, W. W. Jacques patented a cell which excited a good deal of interest at that time.   This consisted of a gas-heated iron pot containing a melted mixture of potassium and sodium hydrate, into which a carbon rod dipped; air was blown against the iron pot, which formed the positive pole, the idea being that this oxygen would combine with the carbon through the intervening electrolyte and produce a current.   The reaction that takes place in the Jacques cell is not the electrolytic oxidation of carbon, but is the union of hydrogen and oxygen.[3] Hydrogen is the active substance at the carbon electrode, and comes from carbon monoxide as shown by the reaction : $CO + 2 \, NaOH = Na_2CO_3 + H_2$.   The iron cathode acts as an air electrode by means of a small amount of manganese, either in the sodium hydrate originally or dissolved from the iron.   The electrochemical reactions are therefore :

[1] Z. f. Elektroch. **1**, 122 (1894); Z. phys. ch. **9**, 540 (1891).
[2] Bechterew, Z. Elektroch. **17**, 851 (1911). See also E. de Fodor, *Elektricität direkt aus Kohle*, p. 41 (1897).
[3] Haber and Brunner, Z. Elektroch. **10**, 697 (1904); **12**, 78 (1906).

At the anode : $H_2 + 2F = 2H^+$
At the cathode : $2H^+ - 2F = 2H$
$$2H + MnO_4^{--} = MnO_3^{--} + H_2O$$
$$\frac{MnO_3^{--} + O = MnO_4^{--}}{H_2 + O = H_2O.}$$
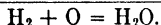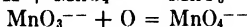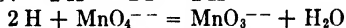
Problem. — Write all the reactions of the cell and show that they add up to the following: $C + O_2 + 2NaOH = Na_2CO_3 + H_2O$.

Bauer, Treadwell, and Trümpler describe a carbon cell consisting of iron wire and iron rust contained in a magnesia crucible placed in a mixture of coke and sodium carbonate held in an iron crucible. Air is blown through a pipe into the iron rust.[1]

In conclusion, it may be said that the chance of finding any solvent in which carbon would dissolve as ions is very remote, and to find one in which both oxygen and carbon would thus dissolve is still more remote ; consequently it seems hardly possible that this problem will be solved by such a direct method.

Others have attempted to construct gas cells consisting of an air electrode and a carbon monoxide electrode. Cells of this kind give electromotive forces corresponding to the reaction $CO + \frac{1}{2}O_2 = CO_2$, using glass as the electrolyte, but they are too easily polarized.[2]

Borchers attempted to use this reaction with a solution of cuprous chloride as the electrolyte.[3] Copper electrodes were used and carbon monoxide was passed over one electrode dissolving as a complex and air over the other. It was hoped that the following reactions would take place :

At the cathode :
$$2Cu^{++} = 2Cu^+ + 2F,$$
$$\frac{1}{2}O_2 + 2Cu^+ + 2H^+ = 2Cu^{++} + H_2O.$$
At the anode : $2Cl^- + 2F = Cl_2,$
$$\frac{Cl_2 + CO + H_2O = CO_2 + 2HCl,}{}$$
Total : $CO + \frac{1}{2}O_2 = CO_2.$
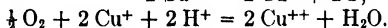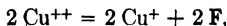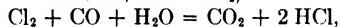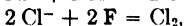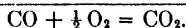
The cell is not capable of furnishing any appreciable current, and carbon dioxide is not produced in detectable amounts.[4]

It seems unnecessary to describe other attempts to construct commercial gas cells.

[1] Z. Elektroch. **27**, 199 (1921).
[2] Haber and Moser, Z. Elektroch. **11**, 593 (1905).
[3] Die Chemische Industrie, **17**, 502 (1894).
[4] Barnes and Veesenmayer, Z. angew. Ch. 1895, p. 101.

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CHAPTER XV

STORAGE CELLS

1. The Lead Storage Cell

Theory

THE lead storage cell, invented in 1860 by Gaston Planté,[1] in the charged state consists of a positive plate of lead peroxide and a negative plate of finely divided lead, both dipping in sulfuric acid of about 1.2 specific gravity. When discharged, the surface of both plates has been changed to lead sulfate. The plates may be brought back to their original condition by sending a current through the battery in the reverse direction.

The reaction taking place in the lead storage cell under ordinary conditions is the following:

$$PbO_2 + Pb + 2 H_2SO_4 = 2 PbSO + 2 H_2O + 43,000 \text{ cal.} \quad (1)$$
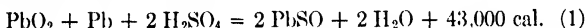
for acid of specific gravity 1.15. This takes place from left·to right on discharge and in the reverse direction on charge. This has been shown by substitution of the heat of this reaction in the Gibbs-Helmholtz equation and calculation of the electromotive force, and by analyzing the amounts of sulfuric acid, lead, and lead dioxide used and of lead sulfate formed for the passage of a given amount of electricity. This reaction is made up of the reactions at the two plates. The lead dips in a saturated solution of lead sulfate and is therefore reversible with respect to the lead ion and the reactions are:

$$\left.\begin{array}{c} Pb + 2 F = Pb^{++}, \\ Pb^{++} + SO_4^{--} = PbSO_4, \\ H_2SO_4 = 2 H^+ + SO_4^{--}. \end{array}\right\} \quad (2)$$
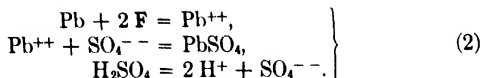
The reactions at the positive plate are not so simple. Le Blanc's explanation is given in the following equations:[2]

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[1] Planté, *The Storage of Electrical Energy*, p. 30 (1877). For the theory of the lead storage cell, see Dolezalek, *Theory of the Lead Accumulator*, translated by von Ende (1904), and for recent studies of the reaction taking place in the cell, MacInnes, Adler, and Jubert, Tr. Am. Electroch. Soc. **37**, 641 (1920), and Knobel, *ibid.*, **43**, 99 (1923).

[2] *Lehrbuch der Elektrochemie*, p. 296 (1922).

$$PbO_2 \text{ (in solution)} + 2 H_2O = Pb^{4+} + 4 OH^-,$$
$$Pb^{4+} = Pb^{++} + 2 F,$$
$$Pb^{++} + SO_4^{--} = PbSO_4, \qquad (3)$$
$$4 OH^- + 4 H^+ = 4 H_2O,$$
$$H_2SO_4 = 2 H^+ + SO_4^{--},$$
$$\text{Total:} \quad PbO_2 + H_2SO_4 + 2 H^+ = PbSO_4 + 2 H_2O + 2 F. \qquad (4)$$
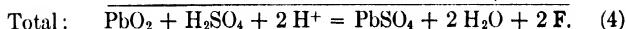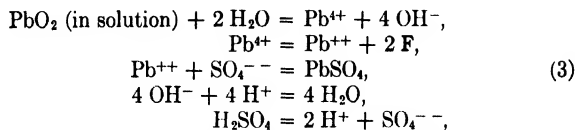
If (2) and (4) are added, equation (1) results.

Liebenow [1] considers the positive electrode to be reversible with respect to the PbO_2^{--} ions:

$$PbO_2, \text{ solid} = PbO_2^{--} \text{ in solution} + 2 F,$$
$$PbO_2^{--} + 4 H^+ = Pb^{++} + 2 H_2O,$$
$$H_2SO_4 = 2 H^+ + SO_4^{--},$$
$$Pb^{++} + SO_4^{--} = PbSO_4,$$
$$\text{Total:} \quad PbO_2 + H_2SO_4 + 2 H^+ = PbSO_4 + 2 H_2O + 2 F.$$
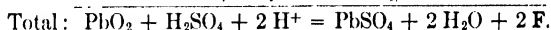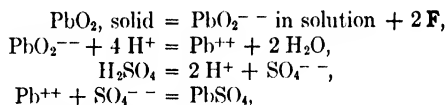
While Liebenow's theory looks simpler than Le Blanc's it cannot represent the reactions that furnish the current on account of the extremely low concentration of the PbO_2^{--} ions, which is calculated to be 4×10^{-53} mol per liter,[2] and it has been shown by Haber that concentrations appreciably smaller than 10^{-7} cannot determine potentials. (See page 102.) The concentration of Pb^{4+} ions in 7.45-n H_2SO_4 is calculated to be 3×10^{-4} mol/l.,[3] which is sufficient to determine a potential.

Problem. — Assuming Liebenow's theory, express the electromotive force of the lead storage cell in terms of electrolytic solution pressures and osmotic pressures, according to the Nernst theory.

TABLE 40

Density of H₂SO₄	Percent H₂SO₄	Electromotive Force at 15° C.
1.050	7.31	1.906
1.150	20.91	2.010
1.200	27.32	2.051
1.300	39.19	2.142
1.400	50.11	2.233

[1] Z. Elektroch. **2**, 420 and 653 (1895).
[2] Dolezalek, *Theory of the Lead Accumulator,* tr. by von Ende, p. 48 (1904).
[3] Cumming, Z. Elektroch. **13**, 19 (1907). For a discussion of the reactions, see Z. Elektroch. **6**, 46 (1899).

The Electromotive Force. — By Le Chatelier's rule, since the acid becomes more dilute on discharging a lead battery, the electromotive force must decrease with decreasing concentration. Table 40 shows the relation between the concentration of the acid and the electromotive force, from direct measurements.

It will be noticed that the electromotive force of the lead storage cell, with the concentration of acid ordinarily used, has the unusually high value of over two volts. Sulfuric acid, if electrolyzed between platinum electrodes, gives a weak evolution of gas at 1.7 volts and at 1.9 a strong evolution. If lead sulphate were spread on platinum, it would therefore not be possible to reduce
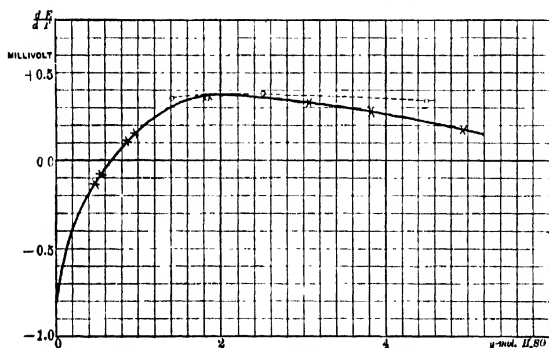
FIG. 116. — TEMPERATURE COEFFICIENT OF ELECTROMOTIVE FORCE OF LEAD STORAGE BATTERY AS FUNCTION OF ACID CONCENTRATION

it to lead and oxidize it to peroxide, for the potential required could not be reached. On lead, however, the overvoltage is so great that the gas evolution does not take place below 2.3 volts, which is greater than the voltage needed to change the sulfate to lead on one electrode and to peroxide on the other. If it were not for this high overvoltage on lead, the lead storage cell would be an impossibility.

The temperature coefficient of electromotive force of the lead storage cell for the concentration of acid used is positive, but on decreasing the concentration of acid the temperature coefficient falls to zero and then becomes negative. This is shown by the curve in Figure 116, representing the results of experiments in which the temperature coefficient was determined between 0° and 24° C. The temperature coefficient is constant in value between 10°

and 70° C. The heavy line in the plot gives the experimental results, and the dotted curve the values calculated from the Gibbs-Helmholtz equation.

Behavior during Charge and Discharge. — If V is the voltage on charging, $\mathbf{E}$ is the open-circuit electromotive force, I is the current, and R is the resistance of the cell, then on charge,

$$V = \mathbf{E} + IR, \tag{5}$$

and on discharge

$$V' = \mathbf{E}' - IR. \tag{6}$$

If the current is kept constant and the value of V is measured at short intervals, the charge and discharge curves obtained are of the form shown in Figure 117. The value of V rises rapidly in the first few minutes of the charge from 2.0 to 2.1 volts, and during the rest of the charge continues to rise slowly, until at the end it suddenly rises to 2.5 to 2.7 volts. During this period of rapid rise in the value of V, the cell begins to evolve gas, after which the value of V changes only slightly. On allowing the cell to stand on open circuit for several hours, the electromotive force $\mathbf{E}$ falls to the value corresponding to the density of the acid. If the cell is then allowed to discharge with the same constant value of the current as used in charging, the value of V' at first falls rapidly to 1.9 volts and then gradually to 1.85 volts, after which it decreases more rapidly to zero. The curves given in Figure 117 were obtained with about 20 percent acid and a current density of about 0.5 amp./sq. dm. of electrode surface. With a greater current density the distance between the charge and discharge curves would increase. The general character of the curves for different makes of cells is the same, though for those having a thin layer of active material the bends are more marked, and for those having a thick layer, they are more rounded.

From the fact that the charging potential V is several tenths of a volt higher than the discharging potential V', as is shown in Figure 117, it is evident there is a loss of from 20 to 30 percent in the energy stored. It might seem at first sight that it is due to the loss of energy due to the resistance of the cell itself, to the IR value in equations (5) and (6), but the value of the resistance of the cell is too small to account for such a large loss. On open circuit the resistance of the smallest cells used is only several hundredths of an ohm, and no large increase in its value takes place when a current is passing. The cause of this loss in energy is the polarization of the electrodes caused by the difference in the
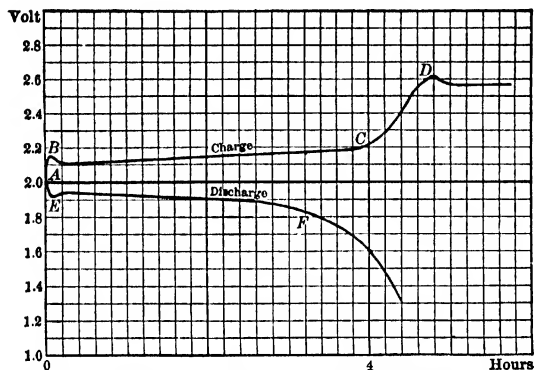
Fig. 117. — Charge and Discharge Curves of the Lead Storage Cell

values of **E** and **E′** due to the change in concentration of the acid in the pores of the plates. On charging, acid is formed in the pores of the plates, where it becomes more concentrated than in the rest of the battery on account of the fact that diffusion does not take place with sufficient rapidity to equalize it. Since the electromotive force of the cell increases with the concentration of the acid surrounding the plates, a higher impressed electromotive force will therefore be necessary in charging. On discharge, the acid is used up in the plates and becomes more dilute than in the rest of the battery, and the voltage falls correspondingly. The charge and discharge curves of the lead cell may now be taken up in detail.

The Charge Curve. — On closing the charging current, sulfuric acid is immediately set free at both electrodes and the electromotive force therefore rises rapidly, as shown by the portion of the curve *A B*. The rate of diffusion increases with the difference in concentration of the acid on the plates and in the rest of the battery, and when concentration difference has become so great that the rate of diffusion and of formation are equal, this rapid increase ceases. The maximum point at *B* is probably due to the destruction of the thin continuous layer of sulfate which forms on the electrodes during rest, thus reducing the resistance of the cell. The slow regular rise to *C* is due to the gradual increase in the density of the acid and also to the deeper penetration of the current lines into the active mass and the corresponding greater

difficulty in equalizing the acid concentration by diffusion. The final rise CD takes place when all of the lead sulfate on the surface of the plates has been used up, and consequently the sulfate does not dissolve rapidly enough to replace that electrolyzed out. Very soon the lead and peroxide ions become so dilute that the work necessary to deposit these ions is equal to that required to produce hydrogen on the cathode and oxygen on the anode. If allowed to stand on open circuit, sulfate diffuses from within the plate and brings back the electromotive force to the normal amount. The maximum point at D is due to the mixing of the concentrated acid in the electrodes with that outside by the gas bubbles.

The Discharge Curve. — In discharge the acid is used up in immediate proximity to the electrodes, and this continues until the concentration difference between the acid in immediate proximity to the electrodes and in the rest of the cell has become so great that diffusion just supplies the quantity used up. During this time the value of V' falls rapidly along AE. The minimum point at E is possibly caused by the formation of a supersaturated lead sulfate solution. The solubility of lead sulfate in a 20 percent solution of sulfuric acid decreases with decreasing concentration, so that at the beginning of the discharge, when little solid sulfate is present, a supersaturation of short duration is probable, and the electromotive force of the battery decreases with increasing concentration of lead ions, as seen from the answer of the problem on page 339. The subsequent gradual fall in the value of V' represented by EF is due to the gradual decrease in the density of the acid in the entire accumulator, but more especially to the greater difficulty in the acid diffusing deeper into the plate as the current penetrates deeper. Finally the rate at which the acid diffuses cannot supply the acid used up by the action of the current, and the value of V' falls off rapidly.

According to this explanation, the loss in energy on charge and discharge is due entirely to the concentration changes that take place in the electrolyte within the active mass. The smaller these concentration changes are, the more nearly will the accumulator approach complete reversibility. This is illustrated in Figure 118. These curves were obtained with a cell of 200 ampere-hours capacity. It is seen that for a current of 0.1 ampere, corresponding to a current density of 0.0017 amp./sq. dm., the charging and discharging potential differ by only 0.006 volt, or 0.3 percent of the electromotive force of the cell, and that by reducing the current this loss may be still further reduced.
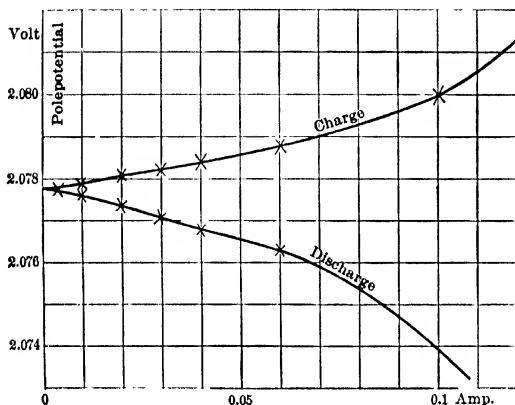
FIG. 118. — VOLTAGE OF THE LEAD STORAGE CELL ON CHARGE
AND DISCHARGE AS A FUNCTION OF THE CURRENT

This loss is not distributed equally between the two plates.

The porosity of the lead plate made from the same sulfate paste as the peroxide is about 1.4 times as great as the peroxide, the potential of the peroxide plate falls off about 1.6 times more than the lead plate for a given change in the concentration of the acid, and finally the concentration change on the peroxide plate is greater than on the lead, because not only is sulfuric acid used up on discharge, but water is also formed. All of these facts tend to make the loss on the peroxide plate greater than that on the lead plate. When the positive and negative plates are made of similar frames and paste, and have approximately the same capacity, it has been found that 60 to 70 percent of the loss takes place on the peroxide plate.

Current Capacity. — The capacity of an accumulator in actual practice means the number of ampere-hours that can be taken from it if discharged to about nine tenths of its original electromotive force, the point where the rapid falling off in the electromotive force takes place. The capacity therefore is determined by the rate of discharge, for the smaller the current the more time the acid has to penetrate by diffusion deeper into the plate, when all of the active material on the surface has been used up. It is also evident that the conductivity of the acid will affect the capacity, for the higher the conductivity the deeper will the current lines be

able to penetrate into the plate. Since there is a density of sulfuric acid at which there is a maximum conductivity, it would be expected that the capacity of a lead storage battery would have a maximum value for this density, and this has been shown experimentally to be the case.

The most important factor in determining the ampere-hour capacity of lead storage cells is temperature. A higher temperature increases the diffusion, the velocity of the reaction, and the conductance of the solution, which allows a deeper penetration into the pores of the plate for a given voltage drop. A change from 8° C. to 48° C. has been found to increase the capacity 300 percent. Greater diffusion is the chief cause of this increase.[1]

The relation between current and time of discharge to a given voltage can be represented by the equation:

$$I^n t = const., \tag{7}$$

where n depends on the character of the plates and varies between 1.35 and 1.72.

Resistance. — The resistances of storage cells vary from a few hundredths of an ohm in the smallest forms used to 10^{-5} ohm for the largest size containing 131 plates of the dimensions 15 by 30 in. About half of this resistance is due to the solution, and half to the plates. An average current for this battery would be 2000 amp. and the loss due to its resistance is:

$$I^2 r = 2000 \times 2000 \times 0.00001 = 40 \text{ watts,}$$

which is only 1 percent of the 3600 watts which the cell is furnishing at 1.8 volts.

Though the resistance is small, there is a large relative increase during discharge, due to the formation of non-conducting lead sulfate. The resistance of the discharged cell may be from two to five times that of the charged cell.

Current and Energy Efficiencies. — The current efficiency of a lead storage cell, or the ratio of the number of ampere-hours obtainable on discharge to the number put into the battery on charge, is from 94 to 96 percent. The small loss of 4 to 6 percent is due to self-discharge and to the small amount of gassing that cannot be avoided. The energy efficiency, on the other hand, which is the ratio of the energy obtainable in the external circuit on discharge

[1] Morse, *Storage Batteries*, p. 135 (1912).

to the energy put into the battery on charge, is only from 75 to 85 percent. The cause of this comparatively low value, as explained above, is the difference between the charge and discharge potential.

Recovery. -- If a cell is allowed to stand on open circuit after charging, the electromotive force falls in fifteen or twenty minutes to the value corresponding to the density of the acid. This is due to solution around the plates becoming saturated with the ions with respect to which they are reversible. On discharge, when the voltage has fallen below the value corresponding to the density of the acid, standing on open circuit brings it back to the normal value. In this case the recovery, as it is called, is due to the diffusion of the sulfuric acid into the pores of the plate where it has become exhausted.

Self-discharge. — If a charged cell is allowed to stand idle, the density of the acid slowly decreases, and the amount of electricity obtainable from it becomes less from day to day. This is known as self-discharge, and for a cell in good condition amounts to from one to two percent a day; if the acid contains impurities, however, it may amount to 50 percent a day. The self-discharge of the lead-sponge plate is more likely to take place than that of the peroxide plate, as it is affected by a greater number of causes. It is fatal for the lead plate if the acid contains any metal more electronegative than lead in contact with sulfuric acid, such as platinum or gold, for the impurity would be precipitated on the plate and produce a short-circuited local element. The lead would then tend to dissolve and deposit hydrogen on the impurity. If the overvoltage of the impurity is not too great, this would in fact take place, and the lead plate would be changed to sulfate. Now the potential of the cell:

$$\text{Pb sponge}|\text{Sulphuric acid}|\text{Platinized Pt} + \text{H}_2$$
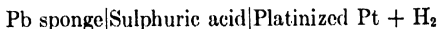
is 0.33 volt, hydrogen being the positive pole. A current could be taken from this cell on closing the external circuit; lead sulfate would be formed on the lead pole and hydrogen would be deposited on the positive pole. But if some metal were substituted for platinum for which the overvoltage is 0.33 volt or more, evidently hydrogen could not be liberated, and no action would take place. Consequently only the metals standing on the left in the following table would be dangerous for the accumulator; those on the right could exist as impurities in the acid without the least danger, even though some of them are more electronegative than lead.

	Over-voltage			Over-voltage
Platinized platinum . . .	0.005	Palladium		0.46
Gold	0.02	Cadmium		0.48
Iron	0.08	Tin		0.53
Platinum, polished . . .	0.09	Lead		0.64
Silver	0.15	Zinc		0.70
Nickel	0.21	Mercury		0.78
Copper	0.23			

As seen from this table, platinum is the most injurious impurity. It has been found that one part of platinum in a million of acid will produce a rapid self-discharge of the lead plate. It has been found, however, that metals when present together can produce a rapid self-discharge, which alone cause scarcely any action. An explanation of this cannot be given at present.

Contamination by platinum can easily occur when sulfuric acid is used that has been concentrated in platinum retorts, and plates once contaminated cannot be made available again. All other metallic contaminations, except manganese,[1] if present only in traces, become inactive on continued use of the cell, probably by gradually alloying with the lead.

The self-discharge of the positive plate takes place more slowly than that of the lead-sponge plate. Metallic impurities are of no effect on the lead peroxide, for they would not be precipitated on it. The only kind of spontaneous discharge is due to local action between the peroxide and the lead of the support, which together form a short-circuited element, and this is of importance only for plates with a thin layer of peroxide.

Another cause of self-discharge of a cell is the presence of salts of metals that can exist in more than one stage of oxidation. For example, an iron salt would be oxidized to the ferric state on the lead peroxide, and would then diffuse to the lead plate and oxidize it to sulfate, thus gradually discharging both plates.

Sulfating. — The plates of a strongly discharged cell on standing gradually become covered with a white coat of lead sulfate. If we attempt to recharge the cell, it is found that the internal resistance has considerably increased, and it does not begin to diminish until the charging current has passed through the cell for some time ; it then gradually approaches its normal value. A test of the

[1] Gillette, Tr. Am. Electroch. Soc. **41**, 217 (1922).

capacity would show that this has lost considerably in value. The phenomenon just described is known as *sulfating*. This is not a very suitable term, since in every discharge sulfate is formed on the plates, which is changed back into peroxide and lead without any difficulty. Elbs explains sulfating as follows: During discharge there is formed on every particle of lead or peroxide a thin layer of finely divided sulfate in contact with an acid solution saturated with the sulfate. If the accumulator is allowed to stand in this condition, and is subject to any variation in temperature, the large crystals will grow at the expense of the smaller ones, for the sulfate increases in solubility as the temperature rises, and the smaller crystals would be used up first, both on account of their size and because the solubility of small crystals is greater than that of large ones. When the temperature falls, the sulfate would be precipitated on the crystals still remaining, and in this way the plate gradually becomes covered with a continuous layer of lead sulfate crystals. Sulfating may be so bad that it is cheaper to replace the plates than to regenerate them by charging.

Construction and Uses of Lead Storage Cells

If two lead plates are placed in dilute sulfuric acid and electrolyzed, a thin film of conducting lead peroxide is produced on the anode which prevents further action of the current, and at the cathode hydrogen is liberated without any effect on the lead. If the circuit is now broken, the lead dioxide and the underlying lead react like a short-circuited battery and produce twice as many equivalents of lead sulfate as there were of lead dioxide. This is called *local action*. A further electrolysis as anode would change the sulfate to peroxide, or if used as a cathode, to spongy lead. Planté's method of formation consisted in charges, discharges, reversals, and rests, and was a slow process. At present two general methods of formation are in use: (1) the accelerated Planté method, and (2) the pasted plate, or the Faure process. This was invented simultaneously by Faure and by Charles F. Brush.

Planté Plates. — In the accelerated Planté process the active material is made from the plate itself. The surface of the plate is first made as large as possible by mechanical means, and this is formed by electrolyzing in a solution of sulfuric acid containing some forming agent, which is a substance that forms a soluble salt with lead. Lead is first dissolved, is precipitated as sulfate, and

is then oxidized to lead dioxide. The process, therefore, differs from the Luckow process, only in the concentration of the anion that forms the soluble salt with lead. If too much were added, the lead sulfate would not stick to the plate ; and if too little, the sulfate precipitates in a dense layer which protects the plate when it becomes peroxidized. Negative plates are made by reversing positives, but must be made to have initially twice their rated capacity because of the increase in size of the grain and consequent loss in surface in the first six months of service.

Some of the forming agents that have been used are : nitrates, acetates, chlorides, chlorates, perchlorates, and sulfites. All of these except perchlorate are destroyed by the current and have to be replaced during formation. Therefore, they can do no harm when the cell is placed in service.

Formation requires 8 to 10 times the number of ampere-hours that the cell is to furnish when in use.

Another method of formation, apparently not used in manufacturing, is to prevent the voltage from rising to 2 volts, at which dioxide is formed.[1] If lead is used as anode at a lower voltage than this, lead sulfate only is formed and this does not protect the plate from further attack. The best way to accomplish this is to hang the plate to be formed in sulfuric acid connected with a charged positive of 8 or 10 times the capacity of the plate to be formed. When the desired thickness of sulfate has been formed, the plate is placed in another cell and oxidized to peroxide with flat lead plates or with sulfated plates which are to be converted into negatives.

Pasted Plates. — The process of manufacturing pasted plates is about as follows : litharge, or red lead, or a mixture of the two, is mixed to about the thickness of putty with sulfuric acid of 1.05 sp. gr. This is forced by wooden paddles into lead-antimony grids, containing 6 to 10 percent of antimony. Sometimes a hardening agent, such as carbolic acid, or a porosity agent, consisting in a soluble salt, like magnesium sulfate, is added to the paste of the positive plate. These are then dried in air for a week, or for a less time in a hot closet. In place of drying, the plates may be soaked in dilute acid for several days.

In this process sulfuric acid forms some lead sulfate, which acts as a cement ; the large crystals of lead sulfate grow at the expense of the small ones and form a network, holding the material in

[1] Ch. Pollak, Germ. Pat. 9166; Dolezalek, *Theory of Lead Accumulator*, p. 193 (1904).

place.   These plates are then electrolyzed continuously for about
four days in sulfuric acid of 1.10 to 1.25 sp. gr.   The negatives
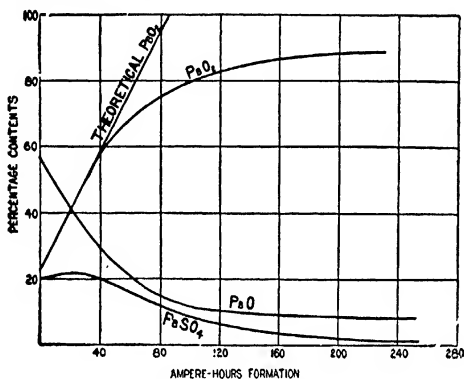
FIG. 119. — FORMATION OF POSITIVE PASTED PLATES

are electrolyzed as cathodes and the positives as anodes.   Figure
119 shows what takes place in the formation of positives, and Figure
120 the same for negatives.   The positive plate evidently has very
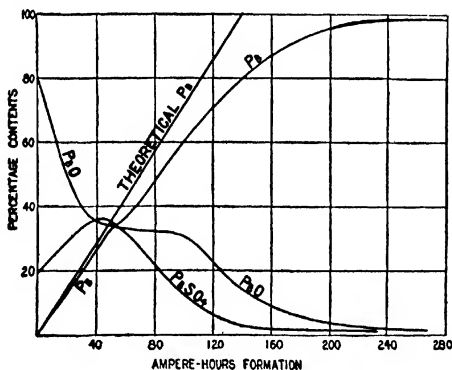
FIG. 120. — FORMATION OF NEGATIVE PASTED PLATES

little lead sulfate left to act as a cement,[1] but this small amount
is all that holds the dioxide in place.   As it cannot exist on the

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[1] Morse, *Storage Batteries*, p 198 (1912).

surface, positive plates are always shedding active material, and this eventually ends the life of the plate.

A different kind of positive is made by the Electric Storage Battery Company, known as the "iron-clad" plate, shown in Figure 121. This consists of a series of perforated vulcanite tubes held in a lead-antimony frame and filled with the active material and a lead rod running down the center for contact. Shedding is less than in pasted plates, but is the cause of the end of the life of this cell, as in other types of cell.

When the formation of negatives begins, it is to be noticed that the formation of lead sulfate takes place rapidly. This is due to the opening of the pores of the plate when lead oxide is changed to lead, so that more sulfuric acid can get at the oxide.

Fig. 121. — Electric Storage Battery Company's "Iron Clad" Positive

The method of making "chloride" negatives once used was to cast lead grids around pellets made of melted lead chloride. The pellets were then reduced to sponge lead.
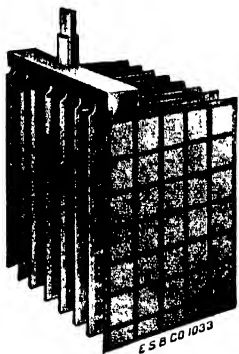
Fig. 122. — Electric Storage Battery Company's "Box" Negative

"Box" negatives now made by the Electric Storage Battery Company (Figure 122), consist of pellets made from litharge and lampblack which are dropped into openings in lead plates and are covered on both sides with perforated sheet lead. These pellets have no coherence and would drop out except for these perforated sheets. When so protected they have good capacity and life. Negative plates do not shed, and for this reason one set of negatives usually lasts as long as two sets of positives.

The plates made by the Salom Battery Company of Philadelphia are made by pressing the formed material in the plates at high pressure; further forming is not necessary. It is claimed by the manufacturers that these plates do not buckle and that they have a higher capacity and longer life than other plates.

Usually negatives are not made by the Planté process, because the box negative is sufficiently rugged for any purpose, and this is combined with a Planté positive, such as the "Manchester" positive shown in Figure 123. The Manchester positive consists of a lead-antimony grid full of holes into which are forced buttons made of corrugated lead ribbon as shown in Figure 124. This is one of the oldest and most used of the Planté plates.

Wooden separators, shown in Figure 125, are generally used to prevent short circuits. Cypress is the best wood for this purpose.

In the Gould cell, both plates are made by the Planté method. A pure-lead sheet is stamped out, and the surface is worked up into the shape shown in cross-section in Figure 126, by rolling the surface

Fig. 123. — Electric Storage Battery Company's "Manchester" Positive

Fig. 124. — Lead Button for Manchester Plate

a number of times with steel disks. This process is called *spinning*. An unspun portion of the plate is left where the wheels stop, forming a number of crossbars in each plate. The plates are then formed as described above. Negative plates are made by reducing peroxide plates.[1] Figure 127 shows a positive plate ready to be formed. The surface of this plate is very large in proportion to its area and is the most efficient in hardest
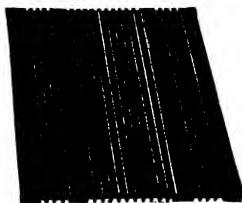
Fig. 125. — Wood Separator for Lead Storage Cell

[1] Catalogues of the Gould Storage Battery Company.

service, but there is a consequent greater danger of buck-
ling.

The Tudor plate, shown in Figure 128, is cast in a mold.   It is
the most used of the European Planté plates, and is made in this
country by the Electric Storage Battery Company.

Many forms of grids are made for pasted plates, some of which
are shown in Figure 129.

Uses. — The principal uses for storage batteries are (1) stand-by
service, (2) regulation, (3) traction, (4) submarines, (5) clock and
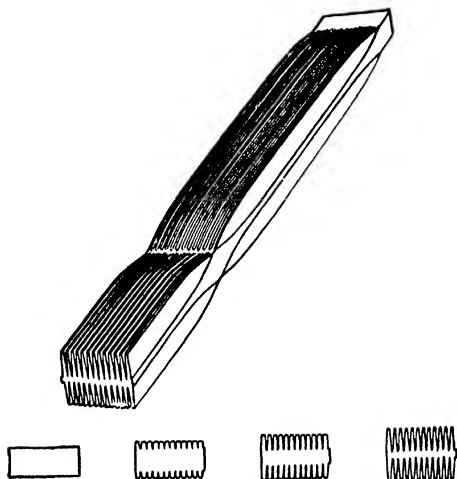
Fig. 126. — Sections of Gould Plate during Spinning

signal systems, (6) operating oil switches, (7) residence and farm
lighting, (8) car lighting, (9) lighting, starting, and ignition in
automobiles, (10) telephone exchanges, (11) for peak loads,
(12) for operating drawbridges, and for numerous minor purposes.
The use in automobiles is probably the largest single use of storage
batteries at present.   In stand-by service a large battery is kept
floating on the line so that in case of accident service will not be
interrupted.   All central power stations are equipped with stand-
by batteries, which are discharged on the average three or four
times a year.   Regulation of trolleys, large factories, etc., is the
hardest kind of service for storage batteries, and requires Planté

positives. Details of wiring are given in electrical engineers' handbooks.

Life of Storage Batteries. — The life of a storage battery depends on the kind of service to which it is put, and is considered ended when the battery has lost 80 percent of its capacity. Table 41 gives the usual period of service for batteries of the Electric Storage Battery Company.
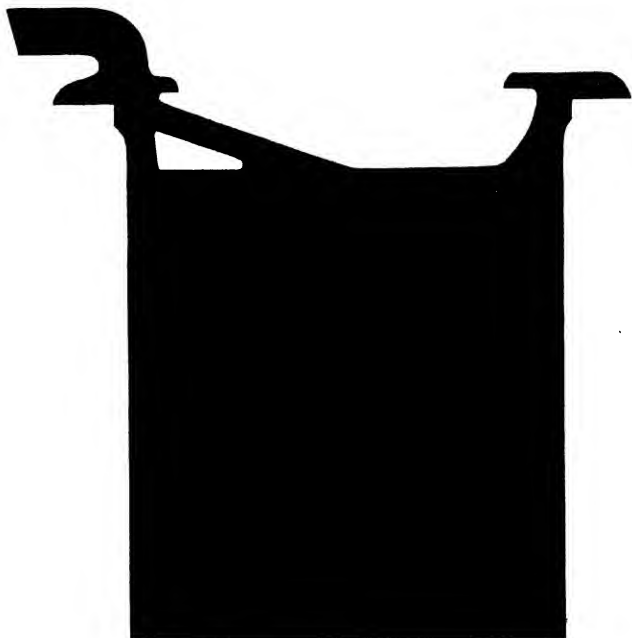
Fig. 127. — GOULD POSITIVE READY FOR FORMING

TABLE 41. LIFE OF STORAGE BATTERIES OF THE ELECTRIC STORAGE BATTERY COMPANY

TYPE	SERVICE	YEARS
XC	Vehicle	2
Iron clad	Vehicle	3
	Car lighting with E. S. B. Co. equipment	10
Chloride: Manchester positive and box negative	Stand-by	15 to 20
	Regulating	5

TABLE 41 — *Continued*

TYPE	SERVICE	YEARS
	Oil switch	8 to 10
	Independent plant	8 to 10
	Clock system and signals	10 to 12
Exide	Oil switch	4 to 5
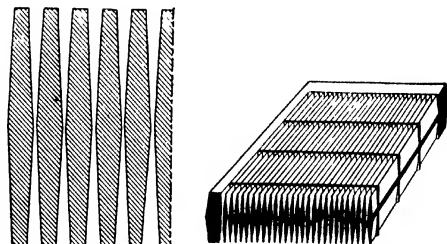
FIG. 128. — TUDOR PLATE

The cost of Exide plates is half the cost of the battery. The cost of a stand-by battery of a power plant supplying a large city may be $1,000,000, and the total maintenance cost per year is 4 percent of the cost of the battery.
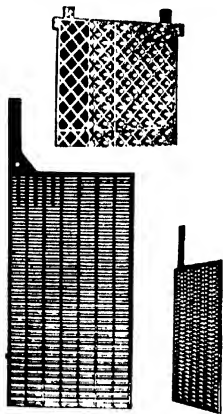
FIG. 129. — GRIDS FOR PASTED PLATES

2. THE EDISON ALKALINE STORAGE CELL

Construction

The Edison storage cell is the only accumulator besides the lead cell that has any commercial importance, and this is not used at all for the heavy work of power plants, but principally for traction. In this cell the active material of the positive pole is an oxide or oxides of nickel, and that of the negative pole, very finely divided iron. The solution is 21 percent potassium hydrate with 50 grams of lithium hydrate per liter. The lithium increases the capacity of the battery 12 percent, but also increases the resistance of the electrolyte 21 percent.[1]

[1] Turnock, Tr. Am. Electroch. Soc. **32**, 405 (1917); Walter E. Holland, El. World, **55**, 1080 (1910).

Edison began to investigate alkaline accumulators in 1898, and after trying a great number of different combinations had the nickel-iron combination fairly well developed in 1900.[1] It then passed through several more stages of development, and arrived in 1904 at what was called the type E 18 battery. This had twelve nickel plates and six iron plates. The active material of each plate was held in 24 perforated nickel-plated steel pockets 7.5 cm. in length, 1.27 cm. in width, and 3 mm. in thickness. The iron plate was mixed with mercury, the effect of which will be ex-

Fig. 130. — IRON ELECTRODES OF THE EDISON STORAGE CELL

plained below, and the nickel oxide with graphite, to increase its conductivity. This cell had two defects: (1) the nickel plate continually expanded on charging and did not contract on discharge, so that the contacts between the active material and the supports became bad, and (2) the graphite mixed with the nickel oxide gradually disintegrated and did not fulfill its function of conducting the current into the interior of the nickel plate, causing the battery to lose its capacity.

[1] Kennelly and Whiting, Trans. Am. Electroch. Soc. 6, 135 (1904).

Both of these difficulties seem to have been overcome in the latest form of this battery, which has been on the market since 1908.   The construction of the iron electrode, shown in Figure 130, has not been altered, and its dimensions are the same as in the E type, but the nickel electrode has been considerably changed.   The nickel plate, shown in Figure 131, was formerly made just like the iron plate, but in the A type [1] it consists of two rows of sixteen round pencils, held in position by a steel frame.   They have flat flanges at the ends by which they are supported and by which elec-
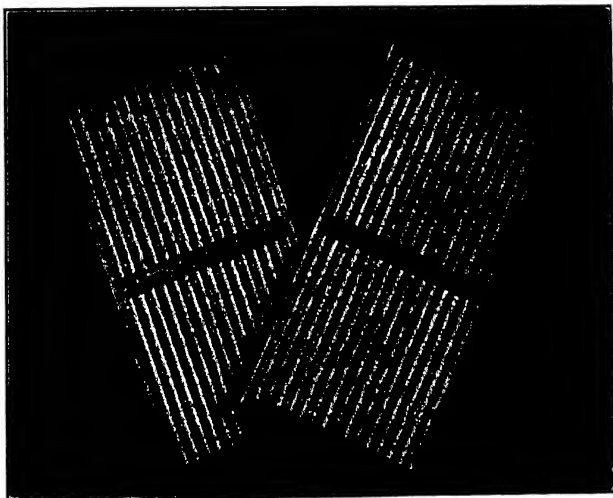
FIG. 131. — NICKEL ELECTRODES OF THE EDISON STORAGE CELL

trical connection is made.   These pencils are perforated nickel-plated steel tubes filled with the active material, 0.65 cm. ($\frac{1}{4}$ in.) in diameter and 10.5 cm. ($4\frac{1}{8}$ in.) in length.   They are put together with a spiral seam to resist expansion, and each pencil also has eight steel rings slipped over it as a further precaution.   The graphite is replaced by nickel made into thin flakes, and distributed in regular layers through the active material, as shown in Figure 132, a section of a pencil taken through its axis.   The dark layers

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[1] Edison cells are designated by a capital letter showing the size of the plate, followed by a numeral showing the number of positive plates.

are nickel flake, and the light-colored layers are the active material. A pencil contains about 350 layers of each kind of material, each layer of active material being about 0.01 in. thick. These pencils are filled under a pressure 2000 lb./sq. in., and are pressed into permanent position in the nickel-plated steel grids by a hydraulic pressure of 40 tons. The negative pockets are filled
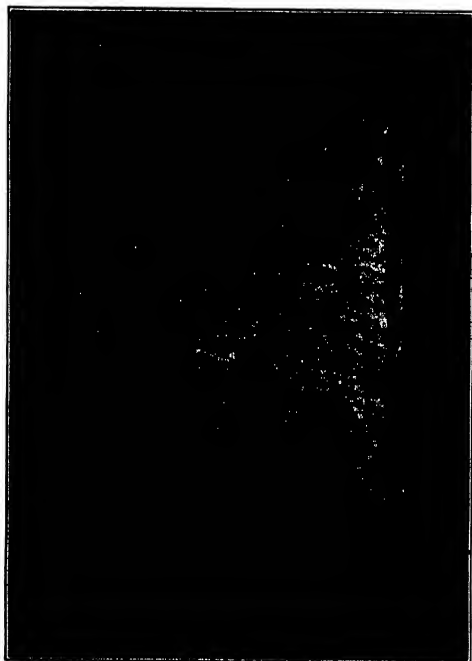
FIG. 132. — ENLARGED SECTION OF PENCIL FROM THE NICKEL
PLATE OF THE EDISON STORAGE CELL

by a method similar to that used for the positives, and are clamped in position with 120 tons pressure.

Type G cells, intended for use where high discharge rates are required, have positive pencils only $\frac{3}{16}$ in. thick and somewhat thinner negatives.

The number of negative plates in all cells is one greater than the number of positives.

Nickelous hydrate is prepared[1] by dissolving shot nickel in sulfuric acid, saving the hydrogen for the reduction of the ferric oxide of the negative plate. The impurities are copper, arsenic, antimony, and iron. Most of the copper is removed by the nickel; what remains is precipitated by hydrogen sulfide together with the arsenic and antimony. This is filtered and the iron is oxidized
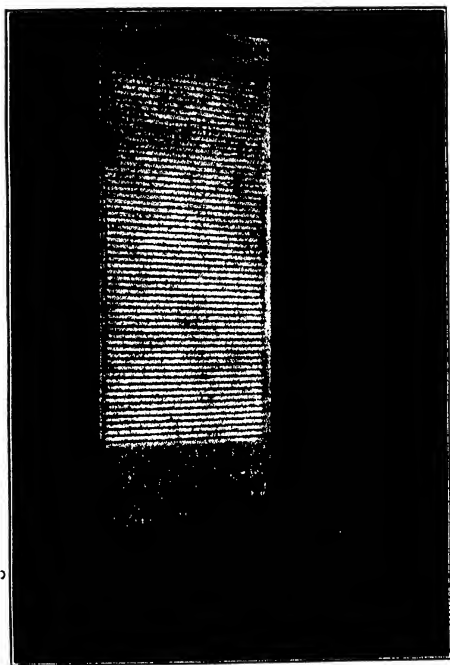
Fig. 133. — Containing Can of the Edison Storage Cell

with bleaching powder or sodium hypochlorite, and is then precipitated as a basic sulfate by carefully neutralizing with soda ash. The purified nickel sulfate is sprayed into a boiling solution of 10 to 15 percent sodium hydrate.   After washing and drying at 100° C. the nickelous hydrate is tested for its electrical capacity and if up

[1] Turnock, Met. Chem. Eng. 15, 259 (1916).

to standard is ground up in 500-pound lots. The material used comes between a 30- and a 190-mesh screen.

The iron used in making the active material of the negative plate is usually a Norway or a Swedish product. This is treated with sulfuric acid in lead-lined digestors. The hydrogen is purified and collected with that obtained in dissolving nickel. The resulting ferrous sulfate is recrystallized several times, dried in centrifugal machines, and then in rotary driers at from 200° to 300° C. It is then given an oxidizing roast in muffle furnaces.
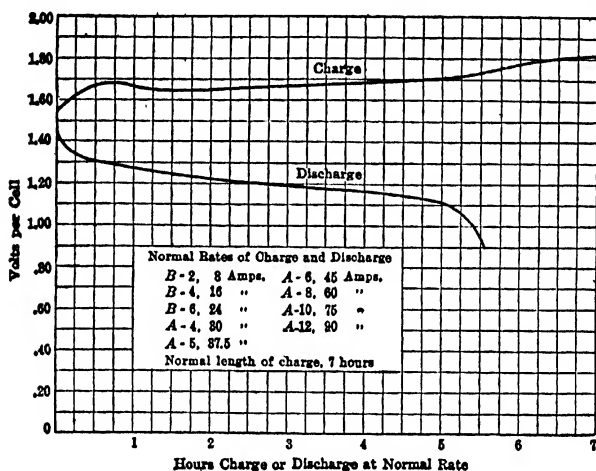
FIG. 134. — CHARGE AND DISCHARGE CURVES OF THE EDISON STORAGE CELL AT NORMAL RATE

After washing the resulting ferric oxide free from sulfate, it is placed in iron retorts set in a muffle furnace and reduced to metallic iron by hydrogen. The product is cooled in hydrogen, and on opening the pan dilute sodium hydrate is run in to prevent rusting. After standing 6 hours it is drained and dried by heat. After grinding and mixing with 6 percent of yellow oxide of mercury it is ready to be tested for electrical capacity.

It requires 4.64 times as much nickelous hydroxide and 5.78 times as much iron as the theoretical amount required by the rated capacity.

Nickel foil is made by the electrolytic deposition of alternate layers of nickel and copper, cutting into pieces $\frac{1}{16}$ in. in square and dissolving the copper with a solution of 25 percent of copper sulfate with 15 g./l. of cupric chloride.[1] As in the earlier cell, the containing can, shown in Figure 133, is of high-grade sheet steel. The container and all other metal parts are heavily nickel plated, inside and out, and are then annealed in hydrogen, thus welding the nickel to the steel. The top of the can is permanently welded in place by the oxy-acetylene flame after the plates are in position. There are four openings in the top, two of which are for the terminals bolted to the groups of positive and negative plates, while the third is for filling, and the fourth contains a valve which al-

FIG. 135. — DISCHARGE CURVES OF THE EDISON STORAGE CELL AT DIFFERENT RATES

lows the gas to escape, but which does not allow any to enter from the outside. The valve is covered with a fine wire gauze to hold back any particles of water coming off with the gas during charging.

Newly assembled cells are given four complete cycles of charge and discharge to form them. Cells with positive tubes $\frac{1}{4}$ in. in diameter are made in twelve different sizes, with capacities from 18 to 450 amp.-hr.

The average discharge voltage for any type is 1.2 volts, when discharged to 1 volt. The charge and discharge curves are shown in Figures 134 and 135. As will be explained below, the capacity can be considerably increased by overcharging. According to the catalogue of the Edison Storage Battery Company, the normal

[1] Met. Chem. Eng. **11**, 162 (1913).

capacity of these cells can be increased 30 percent when charged at the normal rate for ten hours. The continuous rate of discharge may be 25 percent above the normal rate without injury, and for occasional short intervals it may be four times the normal rate. A cell may stand unused for any length of time without injury, but it is said to be better to leave it discharged in this case. As stated above, this must never be done in the case of a lead storage cell.

After standing idle for two months cells can be restored to full capacity by the following treatment.[1] Discharge at the normal
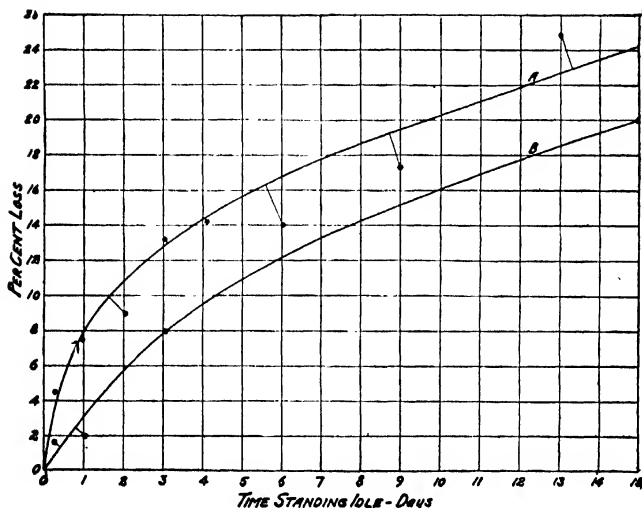
FIG. 136. — SELF-DISCHARGE OF THE EDISON STORAGE CELL (A) AND OF THE LEAD STORAGE CELL (B) AT 22° C.

rate through a suitable resistance to as near zero voltage as possible, and short-circuit for at least 5 hours. Charge at the normal rate for not less than 15 hours, and discharge at the normal rate to as low a voltage as possible, not short-circuiting. Charge at the normal rate for not less than 12 hours and put in service.

The specific gravity of a 21 percent potassium hydrate solution is 1.200. This may fall to 1.160 without affecting the capacity

[1] Circular No. **92** of the Bureau of Standards, *Operation and Care of Vehicle-type Batteries*, p. 27 (1920).

appreciably.   If the battery is in daily operation, the electrolyte should be changed every 8 to 10 months.   In changing solutions the cell should not be allowed to stand empty more than a few minutes.

According to the makers, the best results are obtained when the cell is kept between 75° and 95° F. (24° and 35° C.) on charge, and the temperature should not be allowed to rise above 105° during charge or 115° during discharge.
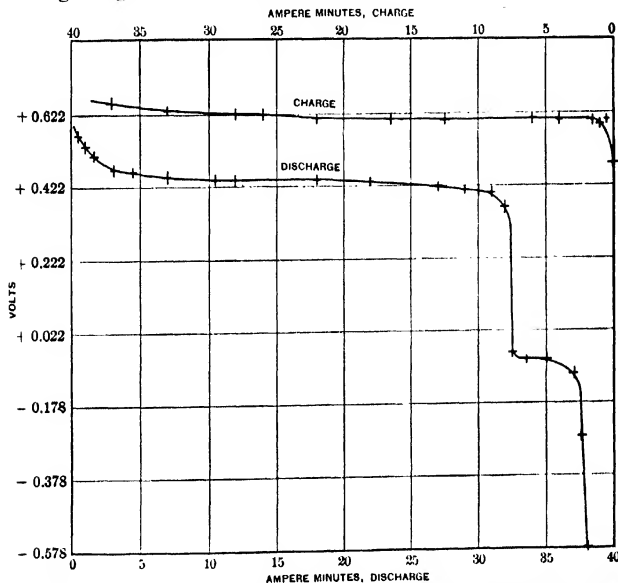
Fig. 137. — POTENTIAL OF THE NICKEL ELECTRODE OF THE EDISON STORAGE CELL IN 2 8 NORMAL POTASSIUM HYDRATE ON CHARGE AND DISCHARGE, REFERRED TO THE NORMAL CALOMEL ELECTRODE AS +0.282 VOLT

If the temperature falls below 50° F. (10° C.) during either charge or discharge, the output and efficiency will be temporarily impaired.

There is a critical temperature below which the Edison cell shows very little capacity.   This temperature depends on the rate of discharge, but for the normal rate it is about 5° C. (41° F.).[1]

The losses in capacity on standing, or the self-discharge, of an Edison cell and a lead cell, are shown in Figure 136.

[1] Bureau of Standards, Circular No. 92, p. 28 (1920).

Theory of the Edison Cell[1]

The Positive Plate. — The active material is put into the positive plate as nickelous hydroxide. On charging, this is first changed to NiO_2, which decomposes slowly with the evolution of oxygen :

$$4\,NiO_2 = 2\,Ni_2O_3 + O_2. \qquad (1)$$
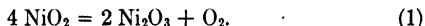
This oxygen is at first completely used up by oxidizing $Ni(OH)_2$ to Ni_2O_3, but as $Ni(OH)_2$ becomes exhausted more and more oxygen escapes.

The change in the potential of the nickel electrode on discharging is shown by the curve in Figure 137. It is of course similar to the discharge curve of the whole battery, since the capacity is determined by this plate. The first part of the curve, concave upward, is due to the discharge of the solid solution of nickel peroxide in nickelic oxide, as is shown by the fact that this part of the curve entirely disappears if the battery stands idle for twelve hours after charging. There is a drop toward the end of the discharge of 0.55 volt to a second discharge process of small capacity, probably due to the oxide Ni_3O_4. This second constant potential becomes shorter as the current density increases, and finally disappears altogether.

The charging potential of the nickel plate is more above the potential corresponding to nickelic oxide than the discharge curve is below. This is because the first action in charging is to produce nickel peroxide, which requires a potential at least equal to that of a solid solution of nickel peroxide. The nickel peroxide at first finds a large amount of nickelous oxide which it oxidizes to nickelic oxide. The nickel peroxide therefore disappears rapidly at first, and with a low current density the potential of the plate is not much above that of nickelic oxide. Gradually, however, the peroxide becomes more concentrated and the potential rises. The nickel peroxide then begins to decompose with the evolution of oxygen, until its rate of decomposition equals its rate of formation. Nickel peroxide is formed also by the electrolytic oxidation of

[1] Zedner, Z. Elektroch. **11**, 809 (1905); **12**, 463 (1906); Elbs, Z. Elektroch. **11**, 734 (1905); Foerster, Z. Elektroch. **11**, 948 (1905); **13**, 414 (1907); **14**, 285 (1908); Faust, Z. Elektroch. **13**, 161 (1907); Foerster and Herold, Z. Elektroch. **16**, 461 (1910); Woost, Dissertation, Dresden (1912); Pattenhausen, Dissertation, Dresden (1914). For an account of Jungner's simultaneous attempt to develop the same reaction, see Foerster, Z. Elektroch. **14**, 286 (1908).

nickelic oxide, so that its formation continues even after all of the nickelous oxide has been oxidized.

The Negative Plate. — The negative or iron plate when charged consists of finely divided metallic iron in the active state. If iron is reduced at a high temperature by hydrogen and then placed in potassium hydrate, it remains inactive, but after electrolyzing for a short while as cathode in a potassium hydrate solution it becomes active and has considerable capacity.

The iron electrode also has two stages in its discharge, as seen in Figure 138. The first consists in the oxidation of iron to ferrous oxide. The second step is due to the oxidation of ferrous to ferric iron, due to the iron becoming passive and the velocity of the
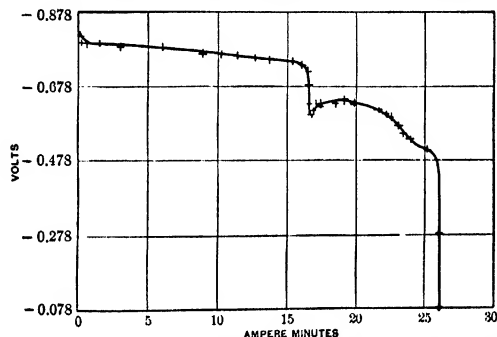
FIG. 138. — POTENTIAL OF THE IRON ELECTRODE OF THE EDISON STORAGE CELL IN 2.85 NORMAL POTASSIUM HYDRATE ON DISCHARGE, REFERRED TO THE NORMAL CALOMEL ELECTRODE AS + 0.282 VOLT

oxidation of metallic iron becoming too slow. The oxidation of iron to ferrous hydrate is then replaced partly or entirely by the oxidation of ferrous to ferric iron. If the ferrous hydrate is not supplied rapidly enough by electrochemical oxidation, the metallic iron is oxidized to the ferrous state by the ferric iron. The result of the second step is, therefore, to change metallic iron to the ferric state. In a 2.85 normal solution of potassium hydrate the potential of the first process is − 0.88 volt referred to the hydrogen electrode as zero, the negative sign referring to the charge on the electrode. The potential difference between the ferro-hydroxide electrode and a 2.85 normal potassium hydrate solution is − 0.75 volt. This difference in voltage between the two steps for the iron electrode is therefore only 0.13 volt, while in the case of the

nickel electrode it is 0.55 volt. This second step is of no practical importance, for the iron plate would not reach it when its capacity is greater than the nickel.

The effect of the addition of mercury to the iron plate is to increase its capacity by keeping the iron in the active state. The beneficial effect of mercury was discovered by Edison empirically, but just how it keeps the iron active is not yet understood. The mercury makes it possible, however, for the plate to have a constant capacity for the first step, independent of the current density, and is therefore of great practical importance. It has no effect on charging. The reason for making the capacity of the iron plate greater than that of the nickel is that the iron electrode should never be discharged as far as the second step, for ferric iron cannot be completely reduced again, and the plates lose in capacity. It has an equally bad effect to allow the iron plate to stand unused in potassium hydrate exposed to the air or to allow it to stand in the air when moist.

In charging, hydrogen is liberated on the iron plate from the start, so that the iron plate causes a greater loss in current than the nickel, on which no gas is liberated during the first part of the charge. It was shown above that the nickel plate changes from $Ni_2O_3 \cdot 1.2\,H_2O$ to $Ni(OH)_2$ on discharging, and the iron plate from iron to ferrous hydrate. These changes may be represented by the equations:

$$Ni_2O_3 \cdot 1.2\,H_2O + 1.8\,H_2O \rightleftarrows 2\,Ni(OH)_2 + 2\,OH^- + 2\,F \quad (2)$$

and
$$Fe + 2\,OH^- \rightleftarrows Fe(OH)_2 - 2\,F. \quad (3)$$
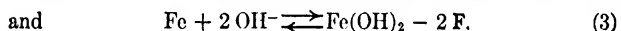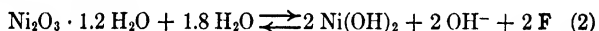
The sum of these equations is

$$Fe + Ni_2O_3 \cdot 1.2\,H_2O + 1.8\,H_2O \rightleftarrows 2\,Ni(OH)_2 + Fe(OH)_2. \quad (4)$$
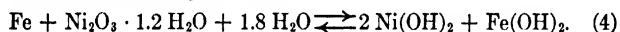
This equation represents the final result in the whole cell on discharge, when taken from left to right, and on charge, when taken from right to left. These equations are not reversible in the ordinary sense, however, for they do not show that hydrogen and oxygen are evolved on charging or that the nickelous hydrate is first oxidized to nickel peroxide. The Edison cell is therefore not strictly reversible, and the equations, though written as reversible, are to be taken only as referring to the initial and final states of the cell.

The Electrolyte. — From the equation (4) it is evident that water is taken up from the electrolyte on discharging by the plates and is given up again on charging. This can be seen by the change

in level in the solution on charging and discharging. According to equation (4), 0.9 mol of water would be combined or set free to one faraday of electricity passing through the cell, and it therefore follows that the electromotive force of the battery will decrease with the increasing concentration of the electrolyte. This is verified by the measurements of the following table:

NORMALITY OF HYDRATE SOLUTION	E M F OF CELL
1.0	1.3510
1.15	1.3368
2.82	1.3377
5.3	1.3349

From what has preceded, it will be evident that the current efficiency and capacity depend on each other. If the battery is not fully charged, the current efficiency will be high, but the full capacity is not obtained. This can be obtained only by charging after gas evolution has begun, which reduces the current efficiency.

The ampere-hour efficiency for all discharge rates is 82 percent, while the watt-hour efficiency for the normal 7-hour rate is 60 percent.[1]

Points of Similarity between the Edison and the Lead Storage Cell. — It is to be noted that in the only two storage cells made, (1) the active material is very slightly soluble in the electrolyte, (2) the current is carried through the main body of the electrolyte by different ions from those which pass back and forth at the electrodes. That is to say, a storage battery must be *mechanically reversible*,[2] and it is for this reason that a Daniell cell would not be successful as a storage cell, although the chemical reaction is reversible.

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[1] Edison Storage Battery Company data sheet No. 5.
[2] Morse, *Storage Batteries*, p. 247 (1912).

CHAPTER XVI

APPLICATIONS OF ELECTRO–OSMOSIS — COTTRELL PROCESS OF FUME PRECIPITATION

THERE are a number of substances which are difficult to separate from water by filtration, and are not of enough value to dry by artificial heat. A good example is peat, which occurs as a slimy material in many places containing 85 to 90 percent water. It cannot be dehydrated by pressure, as an impermeable, rubber-like layer is produced at the surface which does not allow the passage of water. Count Schwerin found,[1] however, that if peat is placed between a wire-gauze cathode and a plate anode, peat is driven from the cathode to the anode, where it is deposited in a solid crust containing 50 to 60 percent water. This can be air dried to contain 20 to 25 percent water, having a heating value of 4000 to 4500 Cal. per kilogram. One cubic meter of water removed requires about 15 kw.-hr. The current removes about 6000 times as much water as it decomposes. About one fifth of the fuel recovered would have to be used to generate the electricity required for its dehydration by electro-osmosis. The subsequent air drying was found too slow and expensive to make the process a success. It is reported that in the dye industry some dyes, such as alizarine, are successfully dehydrated this way.[2]

This process has been more successful in dehydrating clays. Clay contains many impurities consisting of fine particles of such substances as quartz, iron oxide, and mica. These are separated by stirring up with much water and allowing the particles coarser than clay to settle first, in which process electric forces also come into play. In place of waiting for the fine particles of clay to settle after this purification, the clay is now deposited by electro-osmosis on the anode as a firmly adhering mud.

The cell in which this is carried out is a narrow vat, tapering at the bottom. At the top, extending the entire length, there is a rotating, cylindrical anode of hard lead. The cathode is a half

[1] Z. Elektroch. **9**, 739 (1903); Germ. Pat. 124,509; 150,066; 155,453; 179,086; 179,985; 185,189; 277,900; 279,495.
[2] Count Schwerin, Z. Elek. **9**, 730 (1903); Prausnitz, Z. Elek. **28**, 27 (1922).

cylinder of wire netting. The clay to be cleaned is made up in a separate vessel into a thin mud, and, according to the nature of the clay, some water-glass or humic acid and ammonia or alkali are added to the water. This mud passes through several vessels to separate out the impurities and the coarser clay particles, and then to the osmosis vessel. The clay is thoroughly stirred up as it enters and is deposited on the partly immersed, rotating anode as it passes through. It is removed by a scraper in a layer about half a centimeter thick. Between 75 and 100 volts are applied and the current density on the anode is not over 0.01 amp./sq. cm. The yield is 40 kg./kw.-hr. of purified material containing 35 percent water. The turbid water leaving the cell is used for treating new material. This process is used in a large number of plants in Europe.[1]

Tanning consists in the penetration of tannic acid or some other tanning agent into soaked hides. The first attempt to assist this process electrically was made by Crosse[2] in 1849 who placed zinc and lead electrodes in an ordinary tan pit. Since then the process has been used more or less, but it has not been very successful, probably because tannic acid is oxidized by the current. In experiments carried out with tannic acid and capillaries filled with jelly, Rideal and Evans found that the acid entered the tubes from both ends, indicating that both electro-osmosis and cataphoresis are at work.

The most important of all applications of colloid chemistry is the precipitation of fumes or smoke from smelters. This was first proposed by Hohlfeld in 1824. The pioneer work was later done by Lodge and this was reduced to engineering practice as regards equipment and construction by Cottrell.[3] The method is based on the fact that if pointed electrodes are placed opposite a plate electrode, any small particles suspended between the two take the charge of the pointed electrode and consequently move toward the plate and are deposited on it.

Direct currents are used, obtained from an ordinary lighting circuit by raising its voltage to about 30,000 volts by a step-up transformer and commutating by a special rotary contact maker run by a synchronous motor. The plate electrode is No. 10

[1] This account is taken from Foerster, *Elektrochemie wässeriger Lösungen,* 3d ed., p. 146 (1922).

[2] Fölsing, Z. Elektroch. **2**, 167 (1895); Rideal and Evans, J. Soc. Chem. Ind. **32**, 633 (1913); Met. Chem. Eng. **14**, 542 (1916).

[3] J. Ind. Eng. Ch. **3**, 542 (1911); Annual Rep. Smithsonian Inst., **1913**, p. 653.

sheet iron, and the point electrodes are made by twisting an asbestos or a mica preparation between two iron wires. This gives a large number of fine points of sufficient conductivity for this high voltage, though sometimes a special treatment is necessary to give sufficient conductivity. A large number of these electrodes are hung up in a large flue and the gas to be purified is passed in between them. At the Balaklala smelter of the First National Copper Company the grounded collecting electrodes are 6 inches wide and 10 feet high. Each unit contains 24 pairs of electrodes. From 80 to 90 percent of the suspended matter is removed, amounting to 1 to 6 tons every 24 hours. The average consumption of power for the precipitation plant is 120 kw. The gas treated is 200,000 to 300,000 cu. ft. per minute at 100° to 150° C. The dust deposits on the plate electrodes and is shaken off about every 8 hours; the rapid motion of the gas does not prevent this deposition. (This smelter has been dismantled.)

Alternating currents have an agglomerating effect on small particles, but if alternating currents are used, there is nothing but gravity to make the particles settle.

PART III

ELECTRIC FURNACES AND THEIR PRODUCTS

CHAPTER XVII

GENERAL DISCUSSION OF ELECTRIC FURNACES

Historical and Classification. — The usefulness of electric furnaces in chemical and metallurgical work was demonstrated long before there was a sufficient supply of electricity for their commercial development. The apparatus with which Davy (1778–1829) produced sodium and potassium was a small electric furnace. In 1839 Robert Hare [1] operated by means of a battery an electric furnace in a vacuum under a belljar and produced calcium carbide, graphite, phosphorus, and calcium.

In 1880, after the invention of the dynamo, Sir W. Siemens [2] called attention again to electric heating, and demonstrated the fusion of steel and of platinum in a direct-current arc, where the metal, contained in a crucible, was the positive electrode, and the negative, a carbon rod suspended above the crucible.

The electric furnace was probably first used commercially by the Cowles brothers in 1884 in the manufacture of aluminum alloys. Moissan's researches followed a few years later, in which many new products were discovered. The rediscovery of calcium carbide by Willson in 1892 resulted immediately in the manufacture of this product, and this was soon followed by the other electric-furnace products whose manufacture is described below.

There are two distinct reasons for the use of electric heating. The manufacture of many products requires a temperature higher than can be obtained by combustion, and there is consequently no question of competition with combustion heating. In the second place, electric heating is used in cases where the process is simplified and working conditions improved, as in the manufacture of carbon bisulfide, or where it is more economical, as in the electrothermic reduction of iron ore in Norway, and in brass melting.

Electric furnaces may be classified as follows: (1) arc furnaces, (2) resistance furnaces, and (3) induction furnaces. Arc furnaces may be divided into high-tension arc and low-tension arc furnaces. In resistance furnaces the heat is developed by the passage of the

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[1] Doremus, Tr. Am. Electroch. Soc. **13**, 347 (1908).
[2] J. Soc. Tel. Eng. **9**, 278 (1880); Brit. Ass. Report, 1882, p. 496.

current through some suitable *resistor*. This may be the charge itself, or, if the charge is not a good conductor, a special resistor may be necessary, which is usually imbedded in the charge. In other cases the charge is heated by radiation from an outside resistor. Another type of resistance furnace consists in a liquid bath both heated and electrolyzed by the passage of the current through the bath. In this case a direct current is necessary. Induction furnaces may be divided into high-frequency current and low-frequency current furnaces.

Of course all electric furnaces are essentially resistance furnaces, because the heat is developed in all cases by the passage of electricity through a resistor.

The following table summarizes this classification :

1. Arc { High tension / Low tension   2. Resistance   3. Induction
                                                                          High frequency
                                          ┌──────┴──────┐   Low frequency
                                    Charge conducts   Current con-
                                       current   ducted by spe-
                                          │   cial resistor
                              { With electrolysis
                              { Without

Arc Furnaces. — In order that the relation between the electric discharge used in arc furnaces and other forms of electric discharge may be understood, a brief discussion of the discharge of electricity through gases at atmospheric pressure will be given.

The electric discharge through gases may take a number of different forms, depending on the conditions, such as voltage, current, the shape and material of the electrodes, and the pressure and nature of the gas. This discussion will be confined to air at atmospheric pressure, because no other case is of technical importance.

When the current is gradually increased between two fixed electrodes, the following different discharges take place, in the order of their occurrence : [1]

1. The non-luminous discharge ;
2. The glow, or silent discharge ;
3. The brush discharge, accompanied by a hissing noise, and light purple streamers not joining the electrodes ;
4. The spark discharge ;
5. The high-tension arc ;
6. The low-tension arc.

[1] Cramp and Hoyle, J. Inst. E. E. **42**, 297 (1908).

In all these types of discharge, the current is carried by *ions*, which consist of negatively or positively charged atoms or molecules of gas and of free *electrons*. Electrons are the units of negative electricity, having a mass $\frac{1}{1800}$ that of the hydrogen atom. When an atom or molecule loses an electron it is left with a positive charge, and the electron itself soon becomes attached to a neutral atom or molecule. These positively and negatively charged ions tend to unite, so that ionization would soon be reduced to the small residual amount always present in gases unless continually pro-
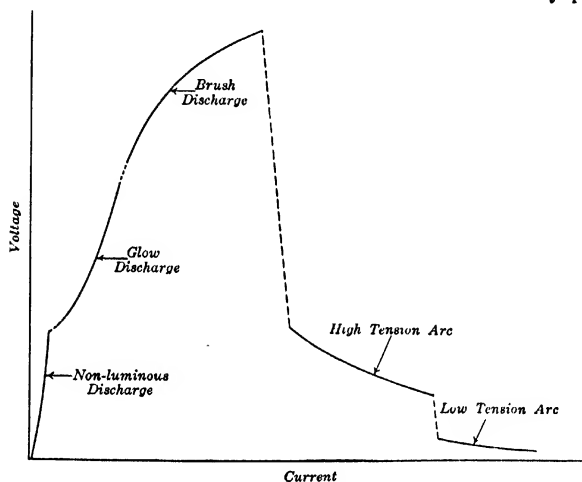
FIG. 139. — CHARACTERISTIC OF ELECTRIC DISCHARGE IN AIR

duced. Some of the principal causes of ionization are: radioactive substances, X-rays, ultra-violet light, chemical action, the impact of ions on atoms, and incandescent bodies. Only impact and incandescence are of technical importance.

The general trend of the *characteristic*, or curve showing the voltage as a function of the current, for the different discharges is represented in Figure 139. On account of the numerous factors that determine the shape of the characteristic to the left of the high-tension arc, that part of the curve is not uniform among different observers,[1] but all agree on the characteristics of the

[1] Toepler, Ann. d. Phys. **7**, 477 (1902); Cady, Tr. Am. Electroch. Soc. **29**, 593 (1916); Brion, Z. Elektroch. **14**, 245 (1908).

high-tension and the low-tension arcs. It must be noted that these curves are not drawn to scale, on account of the great range of values to be represented. The top of the curve may correspond to 90,000 volts, the low-tension arc to 30 volts, while the current in the low-tension arc may be many thousand times that in the high-tension arc.

The curve will now be considered in detail. The non-luminous discharge soon reaches a constant value of current as the voltage increases. This is called the saturation current, and is carried by the few free ions always present. As the voltage increases the ions become sufficiently accelerated to form new ions by impact, the current begins to rise, and the glow discharge appears, separated from the non-luminous discharge by a discontinuous region, represented by the dotted line, in which the conditions are too unstable to make observations. The characteristic of the glow discharge is here represented as positive (that is, increasing current and increasing volts) as given by Toepler, and by Camp and Hoyle. At lower pressures it is stated by Cady to be negative (that is, increasing current and decreasing voltage).

The brush discharge is reached after another discontinuity, which may be accompanied by sparking, as in all discontinuous regions. It may have a positive or a negative characteristic. The glow and the brush discharges are sometimes grouped under the name of *silent discharge*, though the brush discharge is not silent.

When the current reaches a certain value, the conductivity of the air becomes so great, due to ionization by impact, that the voltage drops to a much lower value, passing through a discontinuous gap where the spark discharge takes place, and the high tension arc is formed. This has a negative characteristic.[1]

After another discontinuity, with increasing current, the low-tension arc is formed, which is the kind used in the type of furnace in which calcium carbide is made. It has a much higher temperature than the high-tension arc; the hottest part of the positive carbon is estimated to be between 3900° and 4000° C.[2]

This means that the electrode material is vaporized, and it has generally been assumed that the electrode vapor causes the greater part of the conduction. It has been found, however, that an

[1] For measurements on gaps with maximum values of 9 cm. distance between electrodes, 9000 volts, and 0.09 amp. see Grau and Russ, Sitzungsb. d.k. Akad. d. Wiss. in Wein (II a) **115**, 1571 (1906); **117**, 321, 354, and 364 (1908); Z. Elektroch. **13**, 345 (1907).

[2] Waidner and Burgess, Bull. Bureau of Standards **1**, 123 (1905).

arc may be maintained between tungsten electrodes in nitrogen without consumption of the electrodes;[1] consequently vaporization of the electrodes cannot be a necessary condition for its existence.

In both the high-tension and the low-tension arc, the potential drop between the electrodes consists in a sudden drop at the electrodes and a gradual, uniform drop through the region between. In the high-tension arc the voltage drop is given by the equation,[2]

$$V = a + \frac{bL}{\sqrt{I}},$$

where a is about 350 volts and b is between 100 and 150 and L is in centimeters. Here the drop is greater at the *cathode*, 300 volts of a being due to the cathode and 50 to the anode. The anode and cathode drops for the low-tension arc between solid-carbon electrodes are given by the following formulæ:[3]

$$\text{Anode} = 31.28 + \frac{9 + 3.1L}{I} \text{ volts,}$$

$$\text{Cathode} = 7.6 + \frac{13.6}{I} \text{ volts,}$$

where I is the current and L the length of the arc in millimeters. Here the drop at the *anode* is the greater of the two.

The formulæ connecting the length of the arc with the current and voltage given by Mrs. Ayrton and by Steinmetz[4] apply only up to about 30 amperes, and do not hold for higher values. It has been found that for currents between 300 and 400 amperes and for potential differences of 55 to 20 volts, the potential difference is approximately equal to the distance between the electrodes in millimeters; for currents of about 700 amperes the voltage is less than this distance.[5]

Chemical Effects. — The chemical effects produced by the electric discharge through gases may be either thermal, electrical, or a combination of the two. No doubt photochemical action also takes place, but this may be grouped with the electrical for present purposes. The thermal effect is due merely to the temperature to which the gas is heated; the electrical is due to

[1] Langmuir, Tr. Am. Electroch. Soc. **29**, 609 (1916).
[2] Brion, Z. Elektroch. **14**, 245 (1908).
[3] Mrs. Ayrton, *The Electric Arc*, p. 222. (No date.)
[4] Chem. Met. Eng. **22**, 462 (1920).
[5] Westman, Tr. Am. Electroch. Soc. **43**, 171 (1923).

the splitting up of the atoms as described above and their recombination in some way, without any appreciable change in temperature, and the combined effect is where the electrical effect is modified by the temperature produced by the discharge.

The dark discharge has no chemical effect; this begins to take place only when luminescence appears. A great variety of chemical reactions are produced by the glow and brush discharges, only one of which, ozone formation, is at present of technical importance. Other reactions so produced are:

$$N_2 + O_2 = 2\,NO,$$
$$N_2 + 3\,H_2 = 3\,NH_3,$$
$$C_2H_2 + N_2 = 2\,HCN.[1]$$
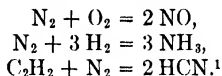
In some cases the spark and the high-tension arc produce the same reactions as the glow and the brush discharge, but in different quantities, as in the cases of ammonia and nitric oxide. Different kinds of electric discharges may, however, produce different reactions: a brush discharge through a mixture of methane and nitrogen gives ammonium cyanide,[2] while the high-tension arc gives hydrocyanic acid and free hydrogen.[3]

In general the electric discharge produces an equilibrium in the reacting gases. For example, if a high-tension arc, cooled so as to prevent the thermal equilibrium from destroying the electrical equilibrium, is passed through pure nitric oxide, this will decompose until its concentration reaches the value which would result from a molecular mixture of nitrogen and oxygen subjected to the same discharge. If an electric discharge is passed through a heated gas, the thermal equilibrium overpowers the electrical when the velocity of the thermal reaction becomes appreciable.

Ozone is another example. This is formed from oxygen at a high temperature, but the brush discharge produces a concentration of ozone at room temperature corresponding to the thermal equilibrium at 2000° C. or more. It is consequently unstable and decomposes slowly, eventually reaching the thermal equilibrium concentration.

The question as to whether the mass-action law holds for gas reactions produced by an electric discharge has been investigated in only a few cases. It has been found to hold for the oxidation

[1] Berthelot, 1869; Norton, *Utilization of Atmospheric Nitrogen*, Dep. of Commerce and Labor, Sp. Agents Series No. 52, p. 129 (1912).

[2] Figuier, C. r. **102**, 694 (1886).

[3] Lipinski, Z. Elektrochem. **17**, 761 (1911).

of nitrogen in the high-tension arc [1] but not for ammonia in the brush discharge.[2] Le Blanc and Davies generalize from these facts that if the mass-action law holds, the equilibrium is thermal, if not, that it is electrical.

For heating solid or liquid substances only the low-tension arc at from 30 to 160 volts is suitable, while a high-tension arc is used for gases, on account of its

FIG. 140 — ARC FURNACE

great length and the possibility of exposing a large quantity of gas to its action. These will be described in the chapter on the fixation of atmospheric nitrogen.
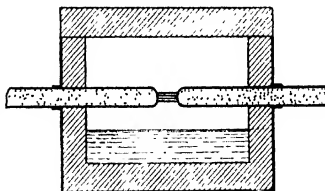
The fundamental types of arc furnaces are shown in Figures 140, 141, and 142. In the furnace represented in Figure 140, the arc is struck directly between the electrodes, heating the charge below by radiation. In the furnaces represented in Figures 141 and 142 the substance to be heated is one terminal of the arc. All arc furnaces belong to one of these types.
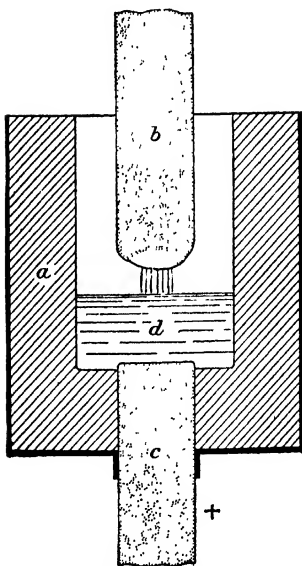
These figures represent single-phase furnaces. A direct current might also be used, though this is not often done. Three-phase furnaces with three electrodes, and two-phase furnaces with three or with four electrodes are built on the same plan.

Resistance Furnaces.— When a charge is a sufficiently

FIG. 141. — ARC FURNACE

[1] Le Blanc and Nüranen, Z. Electrochem. **13**, 297 (1907); Grau and Russ, l.c., note 1, p. 376.
[2] Le Blanc and Davies, Z. Elektrochem. **14**, 361 (1908).

good conductor it can be heated by passing the current directly through it. If it does not conduct well enough for this, it can

FIG. 142. — ARC FURNACE

be heated by packing it around a core consisting of rods of carbon, or of granular carbon, through which a current is sent, as in Figure 143. Finally heat may be radiated from the resistor, as in Figure 144, to the charge below.
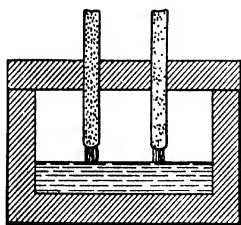
Induction Furnaces. — There are two different types of induction furnaces: those operated on low-frequency currents of 5 to 60 cycles a second, and those using a high-frequency oscillatory discharge.

In the low-frequency furnace, invented simultaneously by Ferranti and by Colby,[1] the metal to be heated is the short-
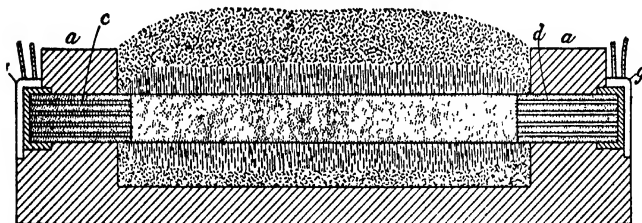
FIG. 143. — RESISTANCE FURNACE WITH CONDUCTING CORE

circuited secondary of a step-down transformer and in the simplest form the secondary is a closed ring of melted metal contained in an

FIG. 144. — RADIATION RESISTANCE FURNACE

annular crucible. If an alternating current is impressed on the primary of the transformer, a secondary current of the opposite phase is induced in the closed ring, depending on the magnitude of the resistance and leakage inductance of the ring and on the voltage induced in it. If the induced voltage[2]

[1] *Electric Furnaces in the Iron and Steel Industry*, Rodenhauser, Schoenawa, and Vom Baur, p. 181 (1920).
[2] The induced voltage E_1 in the primary is equal to the voltage V_1 impressed on the primary minus the resistance and leakage reactance drops in the primary winding.

and number of turns in the primary winding are E_1 and N_1, those in the secondary E_2 and N_2, the following relation holds:

$$\frac{E_1}{E_2} = \frac{N_1}{N_2}.$$

N_1/N_2 is called the ratio of transformation. If the current in the primary is I_1 and that in the secondary I_2, then since $E_1 I_1$ for the primary must equal $E_2 I_2$ for the secondary,[1] it follows that

$$\frac{I_1}{I_2} = \frac{E_2}{E_1} = \frac{N_2}{N_1}.$$

Thus if $N_1 = 100$ and $I_1 = 10$, the current in the iron ring for which $N_2 = 1$ would be $100\, I_1 = 1000$ amperes, and the current in the ring is therefore controlled by regulating the primary current.

Since, except for minor core losses, the power input to the primary of a short-circuited transformer all goes into copper losses in the primary and secondary windings, the power input for the short-circuit condition is:

$$P_1 = \text{power input to the primary}$$
$$= I_1 V_1 \cos \phi_1 = I_1^2 r_1 + I_2^2 r_2,$$

where ϕ_1 is the angle of lag between the current I_1 and the impressed voltage V_1 on the primary. Cos ϕ_1 is called the *power factor* and can be found from the vector diagram.[2] In the case of the induction furnace, $I_2^2 r_2$, which is the power absorbed by the ring, is relatively large compared with the power absorbed by the primary winding, therefore $P_1 = I_1 V_1$ cos ϕ_1 is approximately the power available for heating the ring.

To find an expression for the power factor, start with $OA = I_2$, then $OB = I_2 r_2$, and $BC = I_2 x_2$. E_2 is the voltage induced in the secondary and is represented by OC. $E_1 = a E_2$ is the induced voltage in the primary necessary to produce E_2. To E_1 must be added vectorially $-I_1 r_1$ and $-I_1 x_1$, giving $OD = V_1$, the impressed voltage necessary to produce I_2. From Figure 145,

[1] R. R. Lawrence, *Alternating Current Machinery*, pp. 183-184 (1921).
[2] See R. R. Lawrence, *l.c.*, Chs. XIV and XV.

$$\cos \phi_1 = \frac{OF}{OD} = \frac{aI_2r_2 + I_1r_1}{\sqrt{(aI_2r_2 + I_1r_1)^2 + (aI_2x_2 + I_1x_1)^2}}$$

$$= \frac{I_1(a^2r_2 + r_1)}{I_1\sqrt{(a^2r_2 + r_1)^2 + (a^2x_2 + x_1)^2}}$$

$$= \frac{a^2r_2 + r_1}{\sqrt{(a^2r_2 + r_1)^2 + (a^2x_2 + x_1)^2}}.$$

This equation shows that if r_2 is diminished by increasing the quantity of metal in the melted ring, $\cos \phi_1$ becomes smaller. The same results if the size of the furnace is increased, and the only way to increase the power factor is to use a low frequency, thus lowering the value of x_1 and x_2. In large furnaces the frequency is consequently made as low as five cycles per second.

FIG. 145. — VECTOR DIAGRAM OF LOW-FREQUENCY INDUCTION FURNACE, NEGLECTING MAGNETIZING CURRENT. NOT DRAWN TO SCALE.

NOTATION. — r_1 = primary resistance; r_2 = secondary resistance;
S_1 and S_2 = leakage inductances of primary and secondary windings, respectively;
a = ratio of transformation, or the ratio of the number of turns in the primary and secondary, N_1/N_2. In induction furnaces $N_2 = 1$; and $a = N_1$.
f = frequency;
$2\pi fS_1 = x_1$ = primary leakage reactance;
$2\pi fS_2 = x_2$ = secondary leakage reactance.

There are two ways of placing the primary winding of induction furnaces in relation to the secondary, (1) the disk winding, shown in Figure 146, and (2) the tube winding, shown in Figure 147, as well as various combinations of these two. In the disk winding the coil
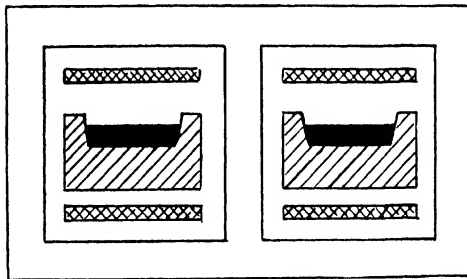
FIG. 146. — DISK WINDING, LOW-FREQUENCY INDUCTION FURNACE

of wire is in the form of a disk above or below the secondary, or both above and below. The object in the disk winding is to get the primary as close as possible to the secondary to decrease the magnetic leakage, while its disadvantage is that it does not permit a general view of the hearth as the tube winding does. Figure 147 represents the Kjellin arrangement of coils, while the Colby arrangement places the coils outside the hearth. The two windings also produce different circulations of the bath on account of their different positions. These circulations are produced by magnetic

FIG. 147. — TUBE WINDING, LOW-FREQUENCY INDUCTION FURNACE

forces, an account of which follows.

  The Pinch Effect.[1] — When an alternating or a direct current passes through a liquid conductor contained in a narrow channel, the conductor tends to contract in cross-section, due to the at-

[1] Northrup, Tr. Am. Electroch. Soc. **15**, 303 (1909); Hering, Tr. Am. Electroch. Soc. **11**, 329 (1907); **15**, 255 and 271 (1909); **39**, 313 (1921).

traction of parallel conductors carrying currents flowing in the same direction. If the current is sufficiently large, wherever there is a slight constriction in the channel a depression will be formed which may reach to the bottom of the channel and completely break the circuit, as shown in Figure 148. As soon as this happens the metal flows together but separates again as soon as the circuit is made. This is known as the *pinch effect*. It causes the circuit to be open such a large part of the time that any metal would freeze up if this were to continue long, and it makes it impracticable to use open channel induction furnaces for melting good conductors such as copper, brass, or aluminum, which would require large currents to melt them.

FIG. 148. — THE PINCH EFFECT

The pressure, P, at the center of a bath of circular cross-section due to the pinch effect is given by the equation [1]

$$P = \frac{(10\ I)^2}{S} \text{ dynes per square centimeter,}$$

where I is the current in amperes and S is the cross-section in square centimeters. The largest currents that can be passed through liquid iron in channels of different sizes are as follows:

DEPTH	WIDTH	CURRENT
2 in.	1 in.	3300 amp.
4 in.	2 in.	9400 amp.
6 in.	3 in.	17000 amp.

Centrifugal Effect. — Since at any instant the current in the primary is opposite in phase to that in the secondary, there will be
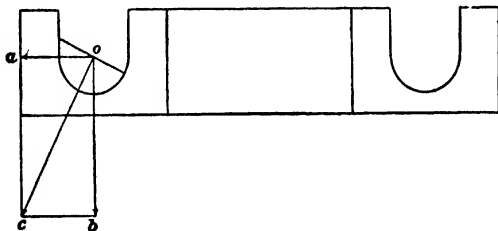
FIG. 149. — THE CENTRIFUGAL EFFECT, INDUCTION FURNACES

[1] Hering, Met. Chem. Eng. 9, 86 (1911).

a repulsion between the two, causing the surface of the melted metal to make an angle with a horizontal plane when there is a tube winding, as shown in Figure 149. Since this same effect would be produced mechanically by rotating the annular bath on its axis, it is called the *centrifugal effect*.[1]

Corner Effect (also called motor effect). — This is the agitation produced in a liquid conductor at a sharp bend, due to the repulsion of the current which flows in opposite directions on the two sides of the bend. The agitation is strongest in the corner where the distance between the conductor on each side of the bend is small. The farther from the corner the less is the agitation.[2]

In three-phase induction furnaces there is a rotating field which drags the metal of the bath after it. This might well be called the motor effect from its resemblance to the induction motor.

The high-frequency induction furnace was invented by Northrup.[3] In this furnace the material to be heated is not in the shape of a ring, as in the ordinary induction furnace, but is held in a crucible placed in the field of a high-frequency coil, and eddy currents produce the heating. Since they increase as the square of the frequency, the reason for using high frequency is evident. If the material to be heated is a non-conductor, a conducting graphite crucible is used. Figure 150 shows the circuits of a single-phase Northrup furnace. A power-factor of 50 percent is easily obtained and 75 percent may be reached under favorable conditions. The spark-gap consists of water cooled copper over mercury in an atmosphere of hydrogen. With the two gaps, in whichever direction the current from the secondary of the transformer is flowing positive current must always leave a mercury surface. When the voltage between the mercury and the graphite reaches a certain minimum value the mercury opens the circuit completely with great suddenness, causing very rapid and regular oscillations. The power input is regulated by raising or lowering the copper electrodes at the spark-gaps. The greater the length of the spark-gaps the greater the power. The crucible and induction coil are shown at *F*. The induction coil is a flattened copper tube cooled

[1] Bureau of Mines Bull., **77**, p. 21 (1916).

[2] Clamer, J. Franklin Inst. **190**, 493 (1920); Northrup, *ibid.*, **190**, 817 (1920); Hering, Tr. Am. Electroch. Soc. **39**, 313 (1921); Brophy, Chem. Met. Eng. **27**, 489 (1922).

[3] Tr. Am. Electroch. Soc. **35**, 69 (1919); **39**, 331 (1921); Gen. El. Rev. **25**, 656 (1922).
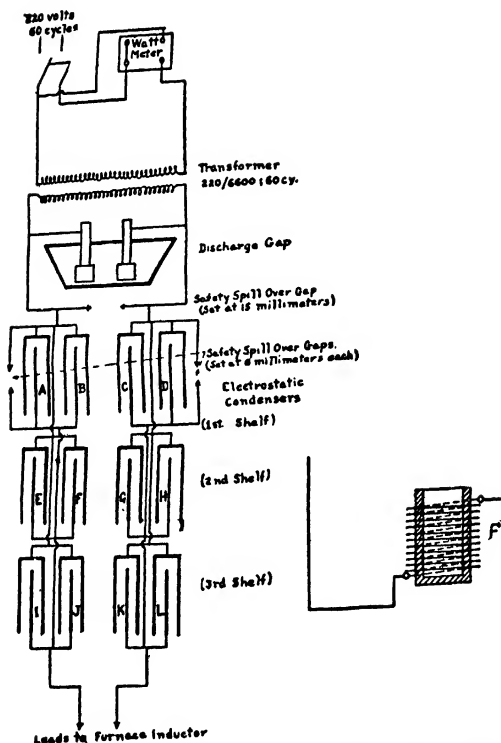
FIG. 150. — AJAX-NORTHRUP HIGH-FREQUENCY INDUCTION FURNACE

by water circulation. The flattening is for the purpose of getting in more turns. The principle cost of the furnace is due to the large condensers required. So far the largest size made takes 60 kilowatts and a charge of 600 pounds of silver.

Efficiency of Electric Furnaces. — The efficiency of furnaces may be defined as the ratio of the heat actually used to heat the reacting substances to the required temperature and the heat absorbed by the reaction to the total heat supplied. The following table gives efficiencies based on this definition.[1]

[1] Stansfield, *The Electric Furnace*, p. 40 (1914).

EFFICIENCIES OF FURNACES FOR MELTING METALS

	PERCENT
Crucible-steel furnaces, fired with coke	2–3
Reverberatory furnaces	10–15
Regenerative open-hearth steel furnaces	20–30
Shaft furnaces (foundry cupolas)	30–50
Large electric furnaces	68–85

This definition is, however, not entirely satisfactory, for in some cases a furnace is used only for holding a charge at a high temperature to allow time for reactions to take place, as in steel refining. If steel were delivered hot to the furnace, according to this definition the efficiency would be zero.

The efficiency of a furnace can always be given in terms of the weight of product per unit of power, and it is common practice to rate electric furnaces in this way, because of its greater practical interest.

The efficiency of electric furnaces increases with their size, consequently there is a tendency to build larger furnaces. For example,[1] the price of packed calcium carbide was reduced from 18 to 20 krone made in small furnaces to 12 to 13 krone per metric ton in 12,000-h.p. covered furnaces under the same conditions. The reasons given by Taussig for this greater economy are (1) simple operation, (2) saving in electrode material and wages, (3) saving in floor space for a given amount of product, and (4) smaller wear and tear of the furnaces. It is also evident that the heat loss must be relatively smaller for large than for small furnaces. This is most simply explained for a spherical furnace, the contents of which are proportional to the cube of the radius and the surface to the square. Consequently if x watt-hours are contained by a unit volume of the charge, the heat content of the furnace will increase as the cube of the radius, and the surface through which it can be lost only as the square, and therefore the larger the furnace the less rapidly can the heat flow away. The same considerations apply to any similarly shaped furnaces of different sizes.

Power Cost. — The cost of electric power in large blocks varies according to the locality. In Norway a horse-power year costs about \$5, while at Niagara Falls it costs from \$15 to \$20, and

[1] Taussig, Int. Congress of Applied Chemistry, **21**, 105 (1912).

at Shawinegan Falls, $12 to $16. Generated by steam in the vicinity of New York, it costs $65.

Electric Furnace Design. — An electric furnace consists of a cavity in which electric energy is changed into heat by one of the methods described above. The material to be heated is placed in this cavity, in some cases filling it completely, in others, only partially. The electric energy is conducted through the walls, roof, or bottom, to the charge by means of electrodes.

The complete design of an electric furnace would include drawings showing the construction of the different parts, consisting of the furnace shell, the lining, the electrodes and holders, the water cooling, the method of feeding the charge and removing the product, an estimate of the output, and of the consumption of power and raw material. The design of furnaces suitable for different products varies considerably with the product to be made, but there are some general considerations applying to all furnaces, and these will form the subject of the rest of the chapter.

Materials for Furnace Linings. — Electric furnaces usually consist of an outer shell of boiler plate lined with refractory material. Some have outer walls of brick, braced, when necessary, with angle irons and tie-rods.

The purpose of the furnace lining is to hold the charge and to prevent as far as possible the loss of heat. The properties desired in furnace linings are (1) a high melting point, (2) resistance to abrasion, (3) mechanical strength, (4) low coefficient of expansion, and (5) low thermal conductance. The term " refractory " includes all these properties. No one material has them all to a satisfactory degree; for example, high melting point is usually associated with relatively high thermal conductivity. Low electrical conductivity is usually desirable for walls and roofs, but a number of steel-refining furnaces depend on having the refractory at the bottom a good electric conductor.

The chemical nature of linings is important, that is, whether acid, basic, or neutral. The lining must of course be of the same nature as the charge, to prevent reaction between the two.

Carbon has the highest melting point of all substances, but is both a good thermal and electric conductor, except in the form of lampblack. Above 2000° C. lampblack is the best of all heat insulators, and is an electric insulator when not strongly compressed.[1] Unlike all other substances that conduct metallically, excepting boron and silicon carbide, the electric conductance of

[1] Northrup, Tr. Am. Electroch. Soc. **39**, 331 (1921).

carbon increases with the temperature. On account of its re-
fractory properties it is used for electric-furnace linings, especially
of furnace bottoms. Air must of course be kept from carbon
linings on account of combustion. They are made of lampblack
or of retort carbon, mixed with tar, heated, and rammed in place.[1]
Such bottoms are used in furnaces for calcium carbide and ferro-
alloys; their life is from two to four years.

Zirconium oxide, the most recently developed refractory, comes
next to carbon in refractory properties.[2] It has a melting point
of about 2950° C. and is chemically inert, withstanding the action
of fused alkalis and fused silica. It has a low coefficient of ex-
pansion (8.4×10^{-7}), and high electrical and thermal resistance.
Its chief future use is as a metallurgical refractory. Its principal
ore is zircon, $ZrSiO_4$, deposits of which are found in Florida.
Zirconium oxide is found in Brazil.

The next most refractory substance is silicon carbide,[3] or car-
borundum, which also goes under the trade names of *crystolon*
and *carbolon*. Four different kinds are on the market: (1) re-
crystallized carborundum, (2) three kinds of bonded carborundum,
consisting of small crystals bonded with refractory mixtures,
(3) various cements for patching, consisting of carborundum and
bonding materials, and (4) *fire-sand*, a by-product consisting of
silicon carbide and partially reduced oxycarbides.

The use of silicon carbide as a refractory was patented by
Benjamin Talbot.[4] No form of carborundum is a good heat
insulator, but crystallized carborundum is a better refractory
than the amorphous fire-sand. Chemically it is neutral.

Bricks and other objects are made of silicon carbide with either
a permanent bond, or with a temporary one.[5] In the second
method the powdered or granular carbide is mixed with a solu-
tion of glue or dextrine, is molded, and is then heated to its
temperature of formation in an electric furnace. The carbide
recrystallizes and is held together by the interlocking of the new
crystals.

[1] Bureau of Mines Bull. No. 77, *The Electric Furnace in Metallurgical Work*,
p. 34 (1916).
[2] J. Soc. Chem. Ind. **36**, 217 (1917); **37**, 734 *A* (1918); Podszus, Z. angew.
Ch. 1917, I, p. 17; Meyer, Met. Chem. Eng. **12**, 791 (1914); **13**, 263 (1915);
anon. *ibid.*, **23**, 770 (1920).
[3] Fitzgerald, Met. Chem. Eng. **10**, 129 (1912); Hartmann, Chem. Met.
Eng. **23**, 769 (1920).
[4] U. S. Pat. 628,288 (1899).
[5] Fitzgerald, U. S. Pat. 650,234 and 650,235 (1900).

Carborundum has high thermal conductance which increases rapidly with the temperature. Its electric specific resistance drops from 50 ohms per centimeter cube at 25° C. to 0.65 ohm at 1400°.[1] Its coefficient of expansion is low (6.58×10^{-6}).

Though carborundum does not decompose in the furnace in which it is produced below 2220° C. it begins to oxidize in an oxidizing atmosphere at 1500°, and reduces metallic oxides at high temperatures. It is decomposed by iron and its slags and by lead oxide. Other metals have no action. It is attacked by sodium carbonate and alkali sulfates or hydrates, by sodium silicate at 1300°, slightly by magnesium oxide at 1800°, and by fused borax or fused cryolite. It is oxidized by fused lead chromate but not by fused potassium chlorate or nitrate. It forms silicides with numerous metallic oxides. Chlorine acts on silicon carbide at 1250° C. with formation of silicon tetrachloride; at 1000° there is scarcely any action. During the war this was used for smoke screens.[2]

The density of silicon carbide 3.2.

A new method of using carborundum has recently been devised, which consists in making a paste of carborundum powder and sodium silicate and painting this on firebricks.[3] The proportions are 75 percent carborundum and 25 percent sodium silicate. A layer of about two hundredths of an inch is applied to the dry brick and is slowly burnt in.

Fused alumina, made from purified bauxite or from emery, is called *alundum*, *aloxite*, or *lionite*. It is made in two forms,[4] a white crystalline product, with less than 1 percent of impurities, consisting of oxides of iron, titanium, and silicon, and a brown product. The white product melts between 2050° and 2100° C., the brown, not more than 50° lower.

Bricks made of this material have shown much longer life as furnace roofs than silica bricks, when not exposed to lime vapors such as occur in a basic-steel furnace slag.

Two allotropic forms of aluminum oxide are known.[5] The α form is the same as the mineral corundum, the second is known as the β form. The α form is the form made in electric furnaces.

[1] Min. Ind. **22**, 10 (1913).

[2] Hutchins, Tr. Am. Electroch. Soc. **35**, 309 (1919); U. S. Pat. 1,271,713 (1918).

[3] Chem. Met. Eng. **24**, 1070 (1921).

[4] Saunders, Tr. Am. Electroch. Soc. **19**, 333 (1911).

[5] Sosman, J. Ind. Eng. Ch. **8**, 985 (1916).

The β form has been patented, but has not yet found any important industrial applications.[1]

Bauxite is very refractory, but must be almost completely calcined before it can be used for furnace lining, or it will shrink excessively; but calcination destroys its plasticity, and it is therefore not often used in electric furnaces.[2] Before calcining it analyzes 60 percent alumina, 30 percent water, and 10 percent iron oxide and silica.[3]

Only one crystalline form of magnesia is known. Its melting point is given by different observers from 1910° to 2800° C.[4] Fused magnesia, either in bulk or as bricks, is used for the bottoms of basic open-hearth furnaces and of basic electric-steel furnaces. One bad property of magnesia bricks is that they crack when heated rapidly to a high temperature. A magnesite lining may be made only of brick dipped in heated tar just before laying in place, or the brick may be covered with ground magnesite which is then heated to a temperature high enough to make it plastic and is worked into a smooth surface with long iron spoons. This gives the best lining but it is not always convenient, in which case a binder is used. This may be hot tar, about 10 percent by weight, or water-glass, or a mixture of 100 parts of fused magnesia, 12 parts of fire clay, and 1 part of borax, all well mixed and wet with about 7 parts of a solution of glucose in water. This should be dried slowly.

Two important sources of magnesite are Styria in Austria, Greece, and the states of Washington and California. From these sources it is between 83 and 86 percent pure; the rest is oxides of manganese, calcium, aluminum, and iron.[5]

Spinel, $MgO \cdot Al_2O_3$, melts at about 2130° C. Bricks of this material give better service than magnesia for doorsills of charging doors.[6]

Silica exists in the three principal forms of quartz, tridymite, and crystobalite. Quartz melts below 1470°, crystobalite at 1625° C.[7]

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[1] Private communication from Mr. L. E. Saunders, Norton Co., Worcester.
[2] Bureau of Mines Bull. 77, p. 33 (1914).
[3] Met. Chem. Eng. **8**, 107 (1910).
[4] Goodwin and Mailey, Phys. Rev. **23**, 22 (1906), 1910°; Le Chatelier and Bogitch, C.r. **165**, 488 (1917), 2400°; Sosman, J. Ind. Eng. Ch. **8**, 985 (1916), 2800°.
[5] McDowell and Howe, J. Am. Ceramic Soc. **3**, 185 (1920).
[6] Chem. Met. Eng. **23**, 770 (1920).
[7] Sosman, J. Ind. Eng. Ch. **8**, 985 (1916).

Three kinds of silica bricks have to be distinguished:[1] (1) With high silica content and with only lime as binder. These are called English dinas, lime dinas, and in America, ganister. (2) With lower silica content and clay as a bond, in England called ganister, in Germany, German dinas, and in America quartzite. (3) Natural dinas bricks, moulded direct from natural rock of mixed quartzite.

These bricks expand considerably on heating, due to the inversion point of quartz at 575° C., which is accompanied by a volume increase in passing from the low to the high temperature. This also has the effect of disintegrating the bricks if heated and cooled repeatedly by this point. Silica bricks are good heat insulators and are used for electric-furnace roofs.

Dolomite is a limestone with a large percentage of magnesia, $CaMg(CO_3)_2$. When burnt and ground so that the largest pieces are not over 10 millimeters, it is mixed with 7 to 10 percent of hot, dry tar and is at once put in place.

Chromite bricks are made from chrome-iron ore, containing 38 to 40 percent Cr_2O_3.[2] This has a melting point of about 2180° C. and is therefore difficult to sinter. For this reason it will not withstand mechanical abrasion and is therefore not suited for furnace bottoms, but only for walls where there is no mechanical wear.

Ordinary firebrick are made of kaolin, $H_4Al_2Si_2O_9$, with a certain amount of extra silica, which lowers the melting point to about 1630° C., that of kaolin being 1820°.[3]

Diatomaceous earth, infusorial earth, or *kieselguhr,* are different names for the silicified remains of small animal organisms, consisting of minute hollow shells. These small air cavities make it an excellent heat insulator.

Nonpareil bricks, made by the Armstrong Cork and Insulation Company, having ten times the thermal resistance of ordinary firebricks are made from diatomaceous earth with a little fireclay and finely ground cork, molded into brick form and fired. The cork is burnt out, leaving the brick very porous. The standard size, $9 \times 4.5 \times 2$ inches, weighs only 1.5 pounds. They will stand a temperature of about 900° C. without alteration.

Sil-o-cel bricks are blocks of diatomaceous earth, just as taken from the mines, cut to the proper shape. They are used for the outer walls of furnaces.

[1] F. T. Havard, *Refractories and Furnaces* (1912).
[2] Bureau of Mines Bull. 77, p. 34 (1914).
[3] Thorpe's *Dictionary of Applied Chem.* **3**, 203 (1922).

Grog is burnt fireclay.   It is mixed with unburnt clay to reduce shrinkage of the unburnt clay.

The following tables give the physical properties of refractory substances.

TABLE 42.   SPECIFIC GRAVITY OF REFRACTORY BRICK

R. M. Howe, Chem. Met. Eng. **23**, 1215 (1920)

Fireclay	2.65–2.75
Silica	2.29–2.44
Magnesia	3.44–3.60
Chrome	3.90–4.00
Carborundum	3.12–3.20
Bauxite	3.15–3.25
Alundum	3.90–4.00
Zirconia	5.0

TABLE 43.   FUSION POINT OF REFRACTORY BRICK

KIND OF BRICK	DEGREES C	AUTHORITY
Fireclay	1615–1715	Kanolt, U. S. Bureau of Stds.,
Silica	1700–1705	Tech. Paper 10 (1912)
Magnesia	2165	" " " "
Chrome	2050	" " " "
Bauxite	1565–1785	" " " "
Zirconia	2563	Ruff and Lauschke, Z. anorg. Ch. 97, 73 (1916).
Zirconia	2600	Arnold, Chem.Ztg.**42**, 413 (1918).
Alundum	2050	Catalog, Norton Company

The fusion point shows the temperature at which a small piece softens under its own weight.   When the influence of pressure as well as temperature is taken into consideration, different results are obtained.

TABLE 44.   BEHAVIOR OF REFRACTORY BRICK HEATED UNDER PRESSURE OF 50 LB. PER SQUARE INCH.

(Quoted by R. M. Howe, *l.c.* above.)

KIND OF BRICK	TEMPERATURE IN DEGREES C.
Fireclay	Softens at 1550
Silica	Rigid at 1500 but probably shears at 1600–1650
Magnesia	Shears at 1410–1555
Chrome	Shears at 1400–1450
Zirconia	Softens at 1510
Bauxite	Softens at about 1350
Carborundum	No signs of failure at 1650, the furnace limit

TABLE 45. ELECTRICAL RESISTANCE OF REFRACTORY
BRICK IN OHMS PER CENTIMETER CUBE

DEGREES C.	MAGNESIA[1]	CHROME[1]	SILICA[1]	FIRE[1]	CARBO-RUNDUM[2]	ALUNDUM[3]
20					50	
528						
600				21,000	14.6	
700				17,000		16 Meg. 730°
800		2800		13,000	7.8	
900		760		9,000		5.3 Meg. 892°
1000		420		6,600	3.7	1.8 Meg. 1020°
1100		430		4,400		
1200		450		2,300	1.3	
1300	6200	410	9700	1,300		
1400	420	320	2400	690	0.65	
1500	55		710	280		
1550	30		22	60		
1565	25		18			

TABLE 46. SPECIFIC HEAT OF REFRACTORY BRICK

(Quoted by Howe, Chem. Met. Eng. **23**, 1215 (1920).)

KIND OF BRICK	AT 100° C.	AT 1000° C.
Fire	0.199	0.253
Silica	0.219	0.298
Magnesia	0.231	0.324
Alundum	0.198	———
Carborundum	0.186	0.31 at 985°

TABLE 47. THERMAL CONDUCTIVITY OF REFRACTORY BRICK AT 1000° C. IN
GRAM-CALORIES PER SECOND PER DEGREE PER CENTIMETER CUBE

(Quoted by Howe, l.c., table above.)

FIRE-CLAY	SILICA	MAGNESIA	CHROME	CARBORUNDUM
0.0039	0.0044	0.0079	0.0057	0.023

[1] This column from Stansfield, McLeod, and McMahon, Trans. Am. Electroch. Soc. **22**, 89 (1912).

[2] This column from Tone, Min. Ind. **22**, 10 (1913). The results of Hartmann, Sullivan, and Allen, Trans. Am. Electroch. Soc. **38**, 279 (1920) are many thousand times larger.

[3] This column from the Norton Company's catalog, quoted by Howe, Chem. Met. Eng. **23**, 1215 (1920).

The Calculation of Heat Loss through Furnace Walls. — If H equals the number of calories conducted in one second through a wall of cross-section S, thickness l, and specific conductance k, when the difference in temperature of the two opposite faces is $t_2 - t_1$ and no heat is lost through the ends of the walls, then

$$H = \frac{kS(t_2 - t_1)}{l} . \tag{1}$$

In the case of a furnace, the cross-section of the wall is not constant, but increases from the inner to the outer surface. It is only when the walls are thin compared to the diameter of the furnace that it is allowable to use the arthmetical or geometrical mean of the inner and outer surfaces for S in formula (1).

The exact calculation of the quantity corresponding to S/l in formula (1), called the *shape factor*, can be carried out for spherical furnaces, with the result:

$$H = \frac{\pi k D d(t_2 - t_1)}{l} , \tag{2}$$

where D is the outer diameter, d the inner, and l is the thickness of the wall. For the curved surface of a long cylindrical furnace,

$$H = \frac{2 \pi k L(t_2 - t_1)}{2.3 \log_{10} \dfrac{D}{d}} . \tag{3}$$

where L is the length, D and d the diameters. Taking into account the two ends by using the geometrical mean of the inner and outer end areas, which is of course an approximation, the entire heat loss would be:

$$H = \frac{2 \pi k L(t_2 - t_1)}{2.3 \log_{10} \dfrac{D}{d}} + \frac{k D d(t_2 - t_1)}{2 l} , \tag{4}$$

where l is the thickness of the end walls. The longer the furnace in proportion to its diameter, the smaller will be the effect of the second term, and the more accurate the formula.

An absolutely exact formula cannot be derived for rectangular furnaces, but the following approximate formula for the shape factor has been determined: [1]

$$\text{Shape factor} = \frac{A}{t} + 0.54 \, \Sigma l + 1.2 \, t, \tag{5}$$

[1] Langmuir, Adams, and Meikle, Tr. Am. Electroch. Soc. **24**, 1 (1913).

where A is the total inner area, t is the thickness of the wall, and Σl is the sum of the lengths of all the inner edges. The last term takes account of the four corners. This formula applies only if all three inner dimensions are greater than $\frac{1}{2}t$, which is practically always the case in electric furnaces, so that it is not necessary to consider here the other cases taken up in the article referred to. The shape factor may be determined experimentally for bodies of any shape by constructing small models of copper and glass and determining the electrical resistance of a saturated copper sulfate solution placed in them.

The following example illustrates the use of formula (5) for a rectangular, electrically heated furnace, of inside dimensions $8 \times 10 \times 20$ inches, with walls 8 inches thick. A is calculated as follows:

$$2 \times 8 \times 10 = 160$$
$$2 \times 10 \times 20 = 400$$
$$2 \times 8 \times 20 = 320$$
$$A = \text{total} \qquad \overline{880}$$

Therefore $A/t = 110$. $\Sigma l = 4 \times 8 + 4 \times 10 + 4 \times 20 = 152$: $0.54 \, \Sigma l = 82$ and the third term is 9.6, whence the shape factor is 201.6. If the shape factor is calculated from the arithmetical mean of the inner and outer surfaces, the result is 354, while the geometric mean gives 274.

The calculation of the heat loss from an electric furnace also involves errors due to lack of knowledge of the values of the other two factors, the temperature difference and the thermal conductance of the walls. The temperatures of the inside and outside surfaces are not uniform, and an average value has to be assumed. The value of the thermal conductivity is also an average value, which may not represent the actual conditions.

Heat Loss through Composite Walls. — In some cases it is desirable to have lining and the outer wall of different materials, each of uniform thickness, for the purpose of better insulation. An air space is not desirable.[1] In a spherical or cylindrical furnace so constructed, the junction of two dissimilar substances would be isothermal surfaces and the resistance to the flow of heat of the composite wall would be the sum of the resistances of the different layers. The resistance to the flow of heat and its reciprocal, the conductance, may be called respectively thermal ohms and thermal mhos.[2] To illustrate this calculation assume

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[1] Bureau of Mines Bull. No. 8, p. 19 (1912).
[2] Hering, Met. Chem. Eng. **9**, 13 (1911); **7**, 11 (1909).

the following data for a spherical furnace whose walls are made of two materials:

d_1 = inner diameter;

d_2 = diameter of sphere formed by the surface of contact of the two materials;

d_3 = outer diameter;

k_1 = thermal conductivity of the inner material; $r_1 = 1/k_1$;

k_2 = thermal conductivity of the outer material; $r_2 = 1/k_2$;

t_1 = temperature of outer surface;

t_2 = temperature of contact surface of the two materials;

t_3 = temperature of inner surface.

The resistance to the flow of heat of the whole wall is

$$R = R_1 + R_2 = \frac{r_1}{(shape\ factor)_1} + \frac{r_2}{(shape\ factor)_2}$$
$$= \frac{r_1 l_1}{\pi d_1 d_2} + \frac{r_2 l_2}{\pi d_3 d_2}$$

by equation (2), where $l_1 = \frac{1}{2}(d_2 - d_1)$ and $l_2 = \frac{1}{2}(d_3 - d_2)$. The value of R having been found, H is given by the equation

$$H = \frac{(t_3 - t_1)}{R}.$$

The temperature t_2 of the contact surface of the two materials may be found from H and the shape factor of either the inner or the outer layer:

$$H = \frac{(t_3 - t_2)}{R_2} = \frac{(t_2 - t_1)}{R_1}.$$

It may be desirable to know this temperature in order to tell whether the material of the outer layer is heated to a temperature too high for it at its inner surface.

A similar calculation may be made for the cylindrical furnace, but for a rectangular furnace, in which the surfaces of the different materials are not isothermals, the calculation would probably be much less accurate.

Furnace Electrodes. — Large-size carbon electrodes are made from calcined anthracite. The details [1] vary, but the principal steps are the following: calcining the coke to remove volatile matter, grinding, mixing with hard and soft pitch, tar, and oil,

[1] Mantell, Chem. Met. Eng. **27**, 161 (1922); Poush, J. Ind. Eng. Ch. **1**, 286 (1909); Clacher, Met. Chem. Eng. **9**, 137 (1911); *The Carbon Electrode,* National Carbon Company, Inc. (1922).

the proportions depending on the character of the carbon required, molding into blocks under pressure, and forcing through dies of the required shape. These " green " carbons are packed in sand and baked at from 1000° to 1400° C. Carbons for graphitizing are made in the same way, except that the raw material is usually petroleum coke. Both carbon and graphite electrodes are threaded electrodes at the ends so that new electrodes can be joined to used electrodes by means of a threaded piece of smaller diameter and a joint compound to fill the space between the point contacts. A broken graphite electrode can be machined, but carbon electrodes are very much harder and are usually not rethreaded if broken. The resistance of a joint is equivalent to that of about a three-inch length of the electrode.[1]

The most recent development in the preparation of carbon electrodes is the Söderberg self-baking, continuous electrode, developed in Norway and recently installed at Anniston, Alabama.[2] This

electrode is made as follows: the mixture, consisting of finely ground coke, partially graphitized anthracite, tar, and pitch, is mixed at 80° C. and is packed in a casing of sheet iron 0.5 to 0.9 mm. thick, of the diameter of the electrode and forming a continuation of this which extends through a concrete floor placed a suitable distance above the furnace. This is where the work of joining new sections of electrode is carried out. As the electrode is eaten away these fresh sections of electrode mixture and containers pass downward to the furnace, becoming gradually hotter, and are usually baked at a small distance above the electrode holder. This casing is prepared in sections and can be joined together as required by welding or riveting. It is melted off in the furnace with the electrode, but the amount is too

Fig. 151. — Söderberg Self-baking Continuous Electrode

small to have any effect on the furnace product. An electrode 85 cm. in diameter carries 23,500 amp. corresponding to 4.5 amp./sq. cm. Figure 151 shows a cross-section of the plant.

[1] FitzGerald and Hinckley, Trans. Am. Electroch. Soc. **23**, 333 (1913).
[2] Richards, Tr. Am. Electroch. Soc. **37**, 169 (1920); **38**, 351 (1920).

The electrical resistance of this electrode cold is 0.007 ohm per centimeter cube, and the specific gravity is 1.5. Its advantages are that it increases the regularity of running electric furnaces, and obviates shut-downs which are necessary for changing the ordinary type of electrode. They are also less expensive.[1]

The Proper Dimensions of Electrodes. — If an electrode is too small in diameter for the current it has to carry, there will be an excessive heating in the electrode itself, causing an unnecessary loss in energy and possible melting of the wall in which it is imbedded; if it is too large, there will be too much heat lost by conduction from the interior of the furnace. The longer the electrode, the less heat will be lost by conduction, but the greater will be the loss due to the electric resistance. There must therefore be a relation between the cross-section and the length of an electrode which will correspond to a minimum loss of power for any given set of conditions. This relation and the corresponding minimum power loss have been worked out by Hering,[2] on the assumption that no heat flows from the electrode to the furnace wall, and that the thermal and electrical conductivities of the electrode are constant. These assumptions are evidently only approximately true. Let

S = cross-section of the electrode,
L = length of the electrode,
I = current of the electrode,
r = electrical resistivity in ohms/cm. cube,
k = thermal conductivity in gram-calories/cm. cube,
T = temperature difference between hot and cold ends,

then for minimum power loss,

$$S = 0.346 \, LI \sqrt{\frac{r}{kT}},$$

and the minimum loss in watts for one electrode = $2.89 \, I\sqrt{krT}$.

In designing an electrode the length will be determined by the thickness of the wall, and in Hering's calculations the length is considered equal to the thickness. Any part that projects inside is considered part of the furnace. Open-top furnaces with the electrodes entering from above are not mentioned, but the length

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[1] Söderberg and Sem, Met. Chem. Eng. **26**, 1178 (1922).
[2] Trans. Am. Electroch. Soc. **16**, 287 (1909); also Electrochem. Met. Ind. **7**, 442 (1909).

may be taken as the distance from the electrode holder to the hot end, if the holder is near the top of the charge. The formula then gives the cross-section.

For example, if the power input of a furnace is 500 kw. at 10,000 amp. and the temperatures at the hot and cold ends of the electrodes are 1700° and 100° C. respectively, to find the minimum loss. For graphite electrodes assume $r = 0.00082$ and $k = 0.29$. The minimum loss $= 2.89 \times 10,000 \sqrt{0.00082 \times 0.29 \times 1600} = 17.8$ kw. The minimum loss for the two electrodes is therefore 7 percent of the total input. Suppose the total length of the electrode is 150 cm. from the inner end to the water-cooled holder outside. The best cross-section would then be

$$S = 150 \times 0.346 \times 10,000 \sqrt{\frac{0.00082}{0.29 \times 1600}} = 690 \text{ sq. cm.}$$

corresponding to a diameter of 29.7 cm.

Problem. — Calculate the ratio of the minimum losses for carbon and graphite electrodes for the same current and temperature using mean values of r and k. The hot and cold ends are at 900° and 100° respectively. See Table 48.

Ans. $\dfrac{\text{Minimum loss for carbon}}{\text{Minimum loss for graphite}} = 1.2.$

That is, the minimum loss for carbon is about 20 percent greater than that for graphite.

As electrodes come in stock sizes, great accuracy in the proportions cannot be carried out in general practice, and as far as concerns loss in energy it is not necessary. For carbon electrodes the conditions may be such that the diameter giving minimum loss would be too large to be practicable. In this case a larger electrode loss would be tolerated in order to make the electrodes of more convenient proportions.

Hering has also proposed a method of determining the average values of k and r. If an electrode is imbedded in the same refractory of which the furnace walls are made and a current is passed sufficient to maintain the center of the electrode at the desired temperature, then

$$r = \frac{SE}{LI} \text{ and } k = 0.119 \frac{EIL}{TS},$$

where S = cross-section of electrode,
  L = length of electrode,
  I = current,
  E = voltage,
  T = temperature difference between the center and ends.

The values in Table 48 have been obtained by this method.[1] The units are centimeters, gram-calories, ohms, and centigrade degrees.

TABLE 48

BETWEEN 100° C AND TEMPERATURE GIVEN BELOW	GRAPHITE		CARBON	
	Heat Conductivity	Electrical Resistivity	Heat Conductivity	Electrical Resistivity
900°	0.291	0.000820	0.129	0.00276
390°	0.339	0.000838	———	———
360°	———	———	0.0890	0.00422

The accuracy of these figures is estimated at a few percent. Later measurements by Hering[2] gave results from which the following Table 49 has been computed. The values of heat conductivity and for electrical resistivity are for centimeter cubes.

TABLE 49

TEMPERATURE, C.°		HEAT CONDUCTIVITY	ELECTRICAL RESISTIVITY
Hot End	Cold End		
		Carbon	
300	40	0.0891	0.00422
701	50	0.124	0.00381
902	60	0.130	0.00377
		Graphite	
355	66	0.339	0.000837
516	70	0.325	0.000827
707	87	0.309	0.000802

The following data were obtained by Hansen.[3] The units are the same as in the table above.

[1] Tr. Am. Electroch. Soc. 16, 315 (1909).
[2] Tr. Am. Electroch. Soc. 17, 166 (1910).
[3] Tr. Am. Electroch. Soc. 16, 329 (1909).

TABLE 50

TEMPERATURE	ACHESON GRAPHITE		NATIONAL CARBON CO.'s ELECTRODES	
	Heat Conductivity	Electrical Resistivity	Heat Conductivity	Electrical Resistivity
25	——	0.00066 to 0.00260	——	0.00287 to 0.0254
Between				
3200 and 200	——	0.00081	——	——
2830 and 30	0.155	——	——	——
3500 and 30	——	——	0.0155	——

The electrical and thermal conductivities of carbon electrodes cannot be determined above 1600°, because on cooling the values do not come back to the original ones, due to a partial conversion of the carbon into graphite.[1] A 1911 catalog of the Acheson Graphite Company gives the electrical conductivity at room temperature of graphite as 0.000126 ohm/cm. cube; of non-graphitic carbon, 0.000488 ohm.

Besides the loss in the electrode itself, a large loss occurs at the contact between the electrode and the cable, due to the contact resistance. This resistance varies with the current density, and where brass clamps are used on graphite it amounts to 0.0117, 0.0045, and 0.0039 ohm/sq. cm. for current densities of 3.7, 5.6, and 7.4 amp./sq. cm.[1]

The values of the thermal conductivity of graphite in Table 51[2] are true values at the temperatures given, not mean values between widely different temperatures. The temperature coefficient differs from the results given above by being positive.

TABLE 51. THERMAL CONDUCTIVITY OF GRAPHITE

DEGREES, C.	GRAM-CALORIES PER CENTIMETER CUBE PER DEGREE PER SECOND
79	0.0371
142	0.0426
261	0.0783
292	0.0919
423	0.1655
535.5	0.2583
555	0.279

[1] Tr. Am. Electroch. Soc. 16, 329 (1909).
[2] Icole, Ann. Chim. Phys. 25, 137 (1912).

The specific resistances of different kinds of granular carbon have been measured by Williams and Shuck.[1] A few of their results are the following:

MATERIAL	SIZE, INCHES		ASH CONTENT	OHMS PER CENTIMETER CUBE	
	Passing Screen with Square Openings of Following Size	Held on Screen with Square Openings of Following Size		20° C.	1000° C.
Acheson graphite . . .	0.5	0.25	0.25	0.069	0.033
National carbon . . .	0.5	0.375	0.45	0.51	0.35
National carbon . . .	0.25	0.125	0.45	0.95	0.37
Retort carbon	0.5	0.25	2.0	0.50	0.33
Charcoal	0.5	0.25	2.5	0.16	0.043

It was also found that the temperature coefficient approaches zero at 1000° to 1200° C. and then becomes positive. According to FitzGerald, at still higher temperatures, it again becomes negative.

The discussion so far has been for the case that the dimensions of the furnace and the power to be applied in order to bring about a desired result are known. If these are not known, an experiment would usually be made on a small scale in order to determine the relation between the size of furnace and the power. There are two cases to be considered, (1) when there is a central core for carrying the current, and (2) when the charge to be heated itself carries the current.

In the first case the heat has to be conducted from the core to the surrounding charge.[2] The rate of this flow is proportional to the difference in temperature of the core and the surrounding charge, the thermal conductivity of the charge, and the surface area of the core. If heat is generated in the core at a given rate, the temperature to which it will rise in a given time will depend on the specific heat of the core and the rate at which the heat flows into the surrounding charge. This rate of flow depends on the area of the core and the conductivity of the charge. Suppose that to bring about the desired reaction in a given charge with a core of a given material experiments are made with a small furnace until the conditions are found under which the desired reaction is brought about. This means that a definite amount of heat must

[1] Tr. Am. Electroch. Soc. **42**, 181 (1922), and the discussion following.
[2] FitzGerald, Electroch. Met. Ind. **2**, 342 (1904).

pass per unit surface of the core, which is a constant for these materials and is independent of the dimensions. If the voltage is E and the current I, the energy in watts per unit surface is $a = \dfrac{EI}{2\pi PL}$, when P is the radius and L the length of the core. Collecting the constants in one factor, this may be written $PL = AEI$. If r is the specific resistance of the core, we also have $\dfrac{E}{I} = \dfrac{rL}{\pi P^2} = B\dfrac{L}{P^2}$. For any furnace of any other dimensions L_1 and P_1, the voltage and current E_1 and I_1 are given by the equations $P_1L_1 = AE_1I_1$ and $\dfrac{E_1}{I_1} = B\dfrac{L_1}{P_1^2}$. From these equations we could solve for the new values E_1 and I_1, if L_1 and P_1 are given. Usually, however, the power is given, and the proper dimensions L_1 and P_1 are desired. Solving for these quantities,

$$P_1 = P\left(\frac{I_1}{I}\right)^{\frac{2}{3}},$$

and

$$L_1 = L\frac{E_1}{E}\left(\frac{I_1}{I}\right)^{\frac{1}{3}}.$$

The following is an example of the use of these formulæ. It was desired to design a 200-kilowatt furnace using a current of 4000 amperes and 50 volts. Experiments on a small scale showed that the right conditions were obtained with 200 amperes at 100 volts and a core 365 centimeters long and 5.1 centimeters in radius. From these values the proper length and radius for the large furnace are found to be 495 centimeters and 37.6, respectively.

For the second case, where the current passes through the charge itself, it is simply necessary to know the amount of heat required to raise a given mass to the desired temperature, that is, the number of watts per unit mass. If the specific heat of the charge is known, this can be computed; if not, an experiment on a small scale with a given mass will determine the energy required.

Where large currents are used, the power factor is made as large as possible by interlacing the leads from the transformer to the furnace and the circuit is made as short as possible, thus giving the minimum amount of inductance.[1]

Regulators. — Electric-arc furnaces are often supplied with automatic regulators, which control electric motors that raise or

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[1] For a method of interlacing, see Yardley, Chem. Met. Eng. **26**, 322 (1922).

lower the electrodes in such a way as to keep the power input as constant as possible. Large fluctuations in power are, however, not eliminated by regulators. Where these are not used, an arc furnace requires constant personal attention, and the switches controlling the motors are thrown one way or the other as required by the indications of the ammeters. The Thury regulator is made by the Westinghouse Electric and Manufacturing Company, and the Seede regulator by the General Electric Company. Each electrode requires a separate regulator.[1]

Uniformity of Temperature in Electric Furnaces. — If the charge consists of a good conductor or of a liquid, the conductivity or the circulation produced by electrodynamic forces will keep the temperature fairly uniform. In case the charge is a solid and not a good heat conductor, it will be more difficult to maintain a uniform temperature, especially if the current is carried by a core. When equilibrium is reached, the rate at which the temperature falls off from the center to the walls will be lower, the lower the thermal conductivity of the walls. If a granular charge carries the current and the charge is under a varying pressure, as it would be in a vertical, cylindrical furnace with one electrode at the top and the other at the bottom, on account of the weight of the charge pressing on the lower portion, the temperature might be considerably higher at the top than at the bottom. This is due to the fact that the resistance of this kind of conductor is lowered by pressure.

If it is desired to heat a non-conducting charge without the use of a core, this may be done by mixing the charge with a good conductor,[2] such as gas carbon. If the gas carbon and the charge are in different sizes, they may be separated after heating by sifting.

Laboratory Furnaces. — It may be useful, before closing this general discussion, to describe a few furnaces suitable for laboratory and research work.

Figure 152 represents to scale an arc furnace that has been used for several years at the Massachusetts Institute of Technology for making calcium carbide and ferroalloys, and for research work. The base is made of half-inch boiler plate, with steel rods inserted for making good contact with the carbon-bottom electrode. This is made by ramming in ground coke mixed with tar. The coke

[1] Rodenhauser, Schoenawa, and vom Baur, *Electric Furnaces in the Iron and Steel Industry*, p. 102 (1920).
    [2] Shoeld, U. S. Pat. 1,317,327 (1919); Thompson, Met. Chem. Eng. **26**, 124 (1922).

should be mixed with some graphite or gas carbon to give it better conductivity. A wooden mold may be used to give the bottom the shape of a crucible. The walls are firebrick, usually not cemented, and held in place by angle irons. The tops are made to order, and consist in two pieces 2 in. thick, so that, when put together, they form a plate 17.5 in. square with a $2\frac{1}{8}$-inch hole at the center. Usually 600 to 700 amp. at 40 volts are used, but sometimes as much as 1500 amp.

For heating large crucibles, the Hoskins Manufacturing Company makes convenient furnaces in different sizes, in which the heat is developed in carbon plates placed on two sides of the cavity. The power input is regulated by the pressure on the plates. The inner walls of the furnace are carborundum plates about 2 inches thick. One of these furnaces is shown in Figure 153. Dixon graphite crucibles are convenient for use in this furnace for ordinary purposes, but if the charge should not come in contact with carbon, a crucible can be made by drilling out an Acheson graphite electrode of the desired size and lining it with ground magnesite moistened with a solution of magnesium chloride as a binder. This is well dried before using.

FIG. 152. — LABORATORY ARC FURNACE; 20 TO 50 KILOWATTS

FIG. 153. — HOSKINS RESISTANCE FURNACE
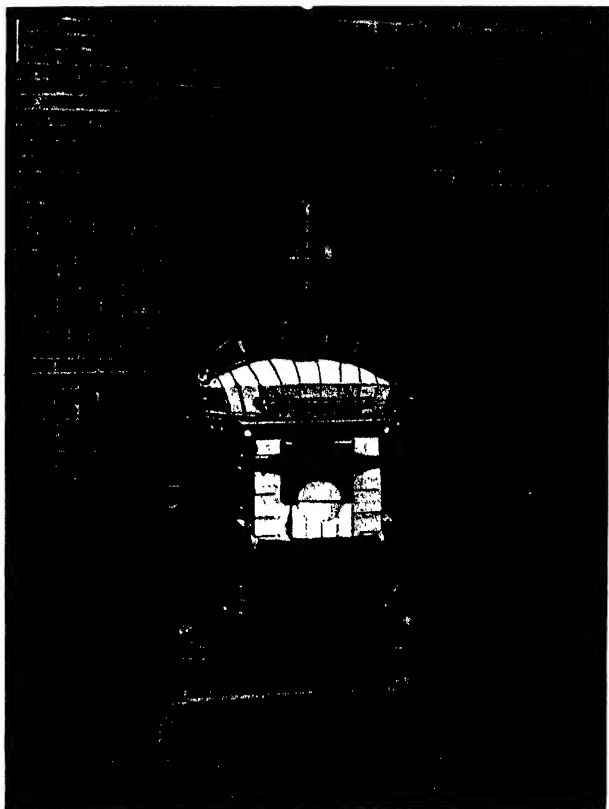
Fig. 154. — Booth Arc Furnace

An arc furnace, shown in Figure 154, capable of holding 200 lb. of steel, is made by the Booth Electric Furnace Company of Chicago. The 2-inch graphite electrodes can be passed through the roof, forming two arcs with the charge, or the electrodes can be passed in through the sides, as in Figure 140, for melting non-ferrous metals. The furnace mouth is in line with the electrodes when in the vertical position.

Induction furnaces holding 50 lb. of iron can be obtained, taking 18 to 20 kw. Annular graphite and clay-mixture crucibles are used. This size furnace is easily started by placing on the cover and passing the flame from a large blastlamp through it for three hours. When it has become red hot 20 lb. of cast iron are poured in. After heating for a while electrically the crucible can be filled by adding solid cast iron. Steel is of course much more difficult to melt.

The Northrup high-frequency furnace, described on page 385, is principally a laboratory furnace, and should be included here.

The Arsem vacuum furnace, shown in Figure 155, is made by the General Electric Company in different types and sizes. The small laboratory size is rated at 15 kw. With a good vacuum 3000° C. may be reached, but at this temperature the heating coil vaporizes rapidly and lasts for only an hour or two. In place of using this furnace with a vacuum, it may be filled with some non-oxidizing gas, such as nitrogen or hydrogen. The presence of a gas lowers the temperature produced by any given power input. This furnace is used principally for research, but a larger size holding a crucible 10 in. high and 4 in. in diameter is built for commercial or for research work. A horizontal vacuum furnace made by the General Electric Company is called the box type. The heater consists of four graphite grids, made by sawing slots in graphite slabs 18 in. long by 5 in. wide by ¾ in. thick. The crucible is box-shaped, 4 in. wide, 12 in. long, and 8 in. high. The temperature limit is 1700° C., while for the large size vertical furnace this limit is 2500° C. Numerous other vacuum furnaces have been devised,

Fig. 155. — Arsem Vacuum Furnace

but the Arsem furnace seems to be the only one that can be bought ready for use.[1]

For a lower range of temperature a convenient type of furnace consists in a tube or muffle wound with a tape or wire of a metal of high melting point, through which a current is sent, as in Figure 156. The winding may be covered with a layer of alundum cement (made by the Norton Company of Worcester) for protection from the air, and is then surrounded with a thick layer of insulating material, such as asbestos-magnesia mixture. These furnaces can be improvised as needed or bought ready made. The Hoskins Manufacturing Company makes a number of such furnaces. Before platinum became so expensive, it was frequently used as the metal winding, but at a little above 1000° C. it vaporizes appreciably. For temperatures up to 1000° C. a chromium-nickel alloy called "nichrome" is now commonly used. Temperatures up to 1600° C. can be obtained by using tungsten or molybdenum wire (made by the General Electric Company) wound on alundum tubes. One of these tubes is placed in an iron box with its ends projecting a sufficient distance to be cooled, the box is then filled with fine silica for insulation and hydrogen is passed through the box to prevent oxidation of the wire. The hydrogen escapes through an exit tube provided in the box and also diffuses through the walls of the tube and comes out its ends, where it is burnt.[2]
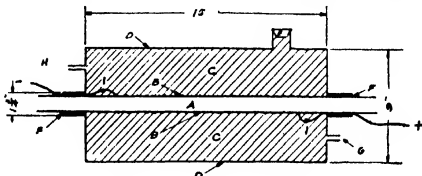
FIG. 156. — TUBE FURNACE

It is not often necessary to regulate laboratory furnaces of this kind automatically, but a regulator consisting of an air thermometer has been used by Bodenstein and Kranendieck.[3]

A convenient resistance furnace for research work that can be constructed at small expense consists in a trough of crushed coke in which a graphite crucible is imbedded. The trough may be

[1] Osterheld, Z. Elektroch. **21**, 54 (1915); Wolf and Mueller, Z. Elektroch. **20**, 1 (1914); Ruff, Z. Elektroch. **20**, 177 (1914); high-pressure furnace. Hutton and Petavel, Phil. Trans. A, **207**, 421 (1908); Weintraub, mercury-arc furnace, U. S. Pat. 997,882 and 997,883; Arsem, Tr. Am. Electroch. Soc. **9**, 147 (1906).

[2] Winne and Dantsizen, Tr. Am. Electroch. Soc. **20**, 287 (1911).

[3] Z. Elektroch. **18**, 417 (1912).

constructed of firebrick, which may be placed in an iron box to hold them securely. Graphite electrodes are imbedded in the two ends of the trough and the top should be covered. The ends of the iron box must have openings cut for the electrodes. Asbestos collars prevent the coke from falling out.

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CHAPTER XVIII

PRODUCTS OF RESISTANCE AND OF ARC FURNACES

Calcium Carbide. — The discovery of calcium carbide is due to Wöhler,[1] who prepared it by the action of carbon on an alloy of calcium and zinc. E. Davy had also produced it in an impure state without identifying it.[2] The commercial importance of calcium carbide, however, dates from its rediscovery by Thomas L. Willson,[3] which was nearly simultaneous with that of Moissan (1892).

The reaction between lime and carbon by which calcium carbide is produced is the following:

$$CaO + 3 C \rightleftharpoons CaC_2 + CO - 125,000 \text{ cal.}$$
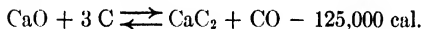
As indicated, this is a reversible reaction, and according to the phase rule has one degree of freedom; that is to say, at a given temperature there is one definite pressure of carbon monoxide which corresponds to equilibrium. At 1475° C. this pressure has been found to be 0.82 millimeter of mercury.[4] Above 1500° calcium carbide decomposes into its elements, but of course not as rapidly as it is produced, otherwise its manufacture would be impossible.

The fact that heat is absorbed when the above reaction proceeds from left to right shows that the equilibrium pressure of carbon monoxide increases with the temperature, and it can be calculated that at about 1840° the pressure equals one third of an atmosphere. In actual practice, however, the partial pressure of carbon monoxide is more than one third of an atmosphere, in which case carbide could be formed at a higher temperature. Taking these facts into consideration, it does not seem probable that 2000° C. is exceeded in actual practice, for high temperature would accelerate the decomposition of the carbide already formed. This explains

[1] Ann. d. Chem. und Pharm. **124**, 220 (1862).
[2] Lieb. Ann. **23**, 144 (1837).
[3] Lewes, *Acetylene*, p. 24 (1900).
[4] Thompson, Proc. Am. Acad. **45**, 431 (1910); also Met. and Chem. Eng. **8**, 327 (1910).

the fact that a resistance furnace, in which the temperature is lower than in the arc, gives better yields than an arc furnace [1] in small-scale work. It is doubtful whether this would hold in large furnaces.

There is also a decomposition according to the reaction:

$$CaC_2 \rightleftharpoons CaC + C$$
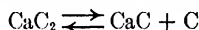
taking place above 1000° C.[2] This subcarbide does not react with water but does absorb nitrogen, and consequently its existence as an intermediate product in the formation of calcium cyanide seems probable.

Commercial calcium carbide is dark colored and crystalline but if pure it is colorless and transparent.[3] It has a density at 18° of 2.22, and is insoluble in all known solvents. It is a powerful reducing agent. If heated with metallic oxides, it gives, according to circumstances, an alloy of the metal in question with calcium or the metal itself, probably according to the reaction:[3]

$$3\,M_2O + CaC_2 = CaO + 3\,M_2 + 2\,CO,$$
$$5\,M_2O + CaC_2 = CaO + 5\,M_2 + 2\,CO_2,$$
or $$2\,SiO_2 + 2\,SiC + CaC_2 = Si_4Ca + 4\,CO.$$
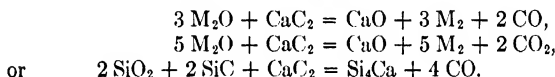
The melting point of pure calcium carbide is not known, but the commercial product of about 80 percent purity melts near 1800° C.[4]

The chief uses of calcium carbide are the production of acetylene according to the reaction

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2,$$
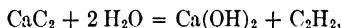
and for the fixation of nitrogen as calcium cyanamide. Acetylene is used for illumination, for cutting and welding by the oxyacetylene blastlamp, and as the starting point for the production of organic compounds, such as acetic acid and acetone.[5]

Materials Used in the Manufacture of Calcium Carbide. — The raw materials for carbide manufacture are carbon in the form of charcoal, anthracite, or coke, and lime. These are broken up

[1] Tucker, Alexander, and Hudson, Trans. Am. Electrochem. Soc. **15**, 411 (1909).

[2] Erlwein, Warth, and Beutner, Z. Elektroch. **17**, 177 (1911).

[3] Abegg, *Handbuch d. anorg. Ch.* **2**, part 2, p. 121 (1905). Reaction for Si₄Ca communicated by Mr. O. Hutchins.

[4] Lampen, J. Am. Ch. Soc. **28**, 851 (1906).

[5] Chem. Met. Eng. **21**, 578 (1919).

into pieces varying in diameter from one to four inches and mixed before shoveling into the furnace.[1]

Since charcoal contains only about 56 percent of fixed carbon, with 28 percent of volatile carbon and 14 percent hydrogen and oxygen, and since a large part is lost as dust, only about half the weight purchased enters the furnace in a usable condition. It requires large storage space, is expensive, and uses up a large quantity of electrode carbon. On the other hand, a higher output is obtained than with coke or coal; on account of the small ash content the purity of the product is the highest possible, and its low electrical conductivity facilitates the furnace operation. In spite of these advantages it has been nearly universally abandoned on account of its expense.

Anthracite is the only kind of coal that has been found satisfactory. Its ash content should not exceed 4 percent. The sulfur is not usually a serious impurity, because it is easily volatilized in the furnace. It may be present, however, in such a form that it goes into the carbide and thence to the acetylene, where it shows its presence by stopping up the burners or by the damaging effect of sulfur dioxide on the materials in the room where the acetylene is burnt.

Phosphorus is the most serious impurity in anthracite. While the upper limit for it as an impurity is given by some as 0.02 percent, Bingham says that it is safe to use anthracite or coke containing 0.04 percent phosphorus if the limestone contains only traces. Phosphorus appears in acetylene as phosphine.

The best grade of coke is called foundry coke, the second grade, blast-furnace coke. The principal disadvantages of coke for carbide manufacture are the high ash and moisture content. The ash should not exceed 12 percent, and is usually at least 8 percent. The moisture is usually about 6 percent, but coke is always dried before use. The advantages of coke are that the furnaces start more easily and work more easily than with anthracite, and the electrode consumption is less. Coal often contains iron pyrites, which may produce as much as 2 percent iron oxide in the coke. This results in the formation of ferrosilicon in the furnace, with the silicon from the lime. In ingot furnaces ferrosilicon remains distributed through the carbide and causes no trouble, but in tapping furnaces it collects at the bottom and from time to time runs out with the tapped carbide. If it escapes detection and

[1] Bingham, *The Manufacture of Carbide of Calcium,* p. 60 (1916); Askenasy's *Technische Elektrochemie,* **1,** 14 (1910).

removal, it appears as a residue in the used carbide and gives excuse for complaint, and it may cause an explosion by a spark produced by two pieces striking together in a drum of carbide. This danger, however, is considered rather remote.

Both the physical properties and the purity of limestone are important in determining its fitness for carbide manufacture. The structure of limestone should be such that it does not crumble on burning, for dust results in loss in the furnace.

The impurities in limestone to be considered are magnesia, alumina, silica, phosphorus, and sulfur. Limestone loses nearly half its weight in burning, consequently the quantity of impurities in burnt lime will be nearly double that in the limestone. In addition to the troubles mentioned below, impurities cause waste in power.

Limestone suitable for carbide should be at least 97 percent pure calcium carbonate. As much as 1 percent magnesia may be present with the production of good carbide, but it interferes with the furnace operation, especially in tapping furnaces, by reducing the fluidity of the carbide. To avoid this the limestone should not contain more than 0.5 percent magnesia.

Alumina causes less trouble than magnesia, though it also decreases the fluidity. It also forms nitride, which results in ammonia in the acetylene. Helfenstein [1] gives 2 percent as the maximum allowable amount of magnesia and alumina together in limestone.

The presence of silica in limestone lowers the fusion temperature, therefore it increases production and facilitates the operation of tapping furnaces. However, if there is as much as 2 percent silica in limestone and the percent of magnesia is also high, the carbide when treated with water decomposes with great rapidity, producing a high temperature and consequent decomposition of acetylene. The carbon thus set free stops up the pipes and burners. This applies only to those generators in which a small quantity of water is brought in contact with carbide. If silica is intimately mixed with iron oxide, as it is in coke, a larger percentage is allowable, because it is removed as ferrosilicon, but silica in limestone does not form ferrosilicon easily. Therefore limestone should not contain more than 1.2 percent silica.

The amount of phosphorus allowable in limestone depends on that in the carbon used, but should in general not exceed 0.004 percent.

[1] See Askenasy's *Technische Elektrochemie*, **1**, 15 (1910).

Sulfur seldom occurs in limestone except in negligible amounts.

The following summary of the maximum quantities of impurities permissible in limestone for carbide is given by Bingham: 0.5 percent magnesia, 0.5 percent alumina and iron oxide, 0.004 percent phosphorus, 1.2 percent silica, and only traces of sulfur.

The electrode consumption depends on the kind of carbon used in the charge. It is greatest for charcoal and least for coke; anthracite consumes about 50 percent more than coke. Bingham gives the following electrode consumption per 1000 kg. of carbide in a 250-kw. furnace: with charcoal, 92 kg.; with coke, 16.8 kg.; with anthracite, 26.4 kg.

Helfenstein gives the following table of consumption of raw materials for 1000 kg. of packed carbide, made in a tapping furnace:

Coke	. . . .	600 to 700 kg.
or Anthracite	. . . . . .	640 to 700 kg.
or Charcoal	. . . . . .	800 to 950 kg.
Lime	. . . .	920 to 1050 kg.
Electrodes	. . . .	10 to 40 kg.

Calcium-Carbide Furnaces. — Calcium carbide is made in arc furnaces from which it is removed either as a solid ingot or by tapping while liquid. These are called *ingot furnaces* and *tapping furnaces* respectively. The original furnaces used by the Union Carbide Company at Niagara Falls, shown in Figures 157 and 158, were of the ingot type. The lower electrode was a small car which could be removed when filled.

The Horry rotary continuous furnace,[1] introduced in 1898 but since given up, is shown in Figure 159. It consisted of an iron wheel 8 feet in diameter and 3 feet in width with an annular-shaped space around the circumference in which the carbide was formed. The electrodes projected vertically down into this space. As carbide formed it was removed from the electrodes by the rotation of the

FIG. 157. — SECTION OF FIRST CARBIDE FURNACE USED AT NIAGARA FALLS

wheel, and was removed when diametrically opposite the electrodes. This gave sufficient time to cool, since the wheel

[1] Richards, Electrochem. Ind. 1, 22 (1902).

made only one complete revolution a day. Iron plates around the circumference of the wheel held the carbide in place while under the action of the current. These had to be removed before cracking off the carbide. Each furnace took 3500 amperes at 110 volts and produced 4000 pounds of carbide a day.

At present carbide furnaces are always of the tapping variety with a capacity of 5000 to 20,000 h.p. They are usually three-phase. The electrodes are arranged in two ways: (1) all suspended from above, as in Figure 160, or (2) the bottom may be the third electrode. These refer to three-phase furnaces. The removal of one electrode would make these illustrations apply to single-phase current. Three-phase furnaces are usually built with all electrodes above and placed in a straight line. There are as many tap-holes as arcs. The furnace itself consists of a rectangular boiler-plate shell lined with refractory material. On top of this the bottom has a carbon lining to make it conducting. A special electrode is required for melting through the solid carbide at the tap-holes.

The inner walls should be so far from the electrodes that they are not attacked by the high temperature or by the charge. At from one to three feet from the electrodes, depending on the power, no carbide is produced. The walls should be beyond this range. Vertical electrodes should be so far apart that no appreciable current flows between them through the cold part of the charge, as this would be wasted.

Fig. 158. — Section of First Carbide Furnace Used at Niagara Falls
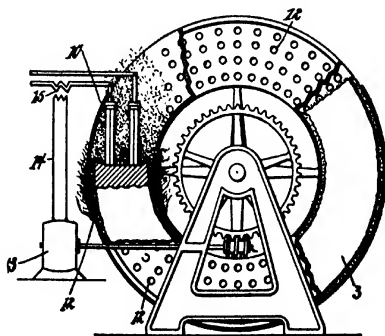
Fig. 159. — Horry Continuous Carbide Furnace
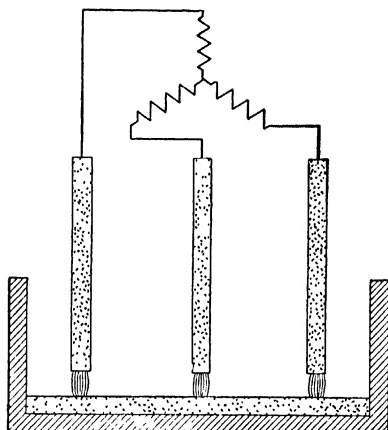
FIG. 160. — SECTION OF THREE-PHASE ARC FURNACE

This distance depends on the voltage and the conductivity of the charge, but may be stated in general to be 2 to 3 meters.

Furnaces are sometimes roofed, as in the Helfenstein furnace in Figure 161, and the gas collected is used for fuel. Bingham gives the following analyses of furnace gases from two closed furnaces: [1]

TABLE 52.   FURNACE GASES FROM CARBIDE FURNACES

	No 1, PERCENT BY VOLUME	No. 2, PERCENT BY WEIGHT
CO_2	0.0	3.12
CO	65.8	82.29
H_2	30.9	1.44
CH_4	2.0	0.83
N_2	1.3	10.4
SO_2		1.92

In general, alternating currents are used, but merely because more convenient than direct currents. The frequency is usually 60 cycles a second, but at Niagara Falls it is 25 cycles. The following are the voltages of different size furnaces:

<div style="text-align:center">

3700 kw. . . . . 100–120 volts

7460 kw. . . . . 130 volts

15,000 kw. . . . . . . 150 volts

</div>

The power factor is 0.8. Safe practice for current density in

[1] *The Manufacture of the Carbide of Calcium*, p. 143 (1916).
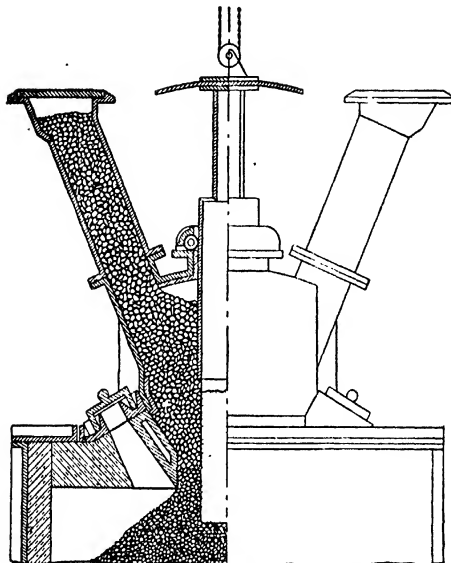
Fig. 161. — Helfenstein Roofed Furnace

the electrodes lies between 5.5 and 7.7 amp./sq. cm. (35 to 50 amp./sq. in.) [1]

The usual production of carbide about 89 percent pure lies between 5 and 6.5 kg. per 24 kw.-hr.

The theoretical yield can be calculated roughly if assumptions are made as to the temperature at which carbide is formed, the temperature of the gas leaving the furnace, and the specific heat of carbide.

The heat required to produce one formula weight of carbide is the following:

(1) Heat absorbed at room temperature by the reaction . . 125,000 cal.

(2) Heat required to raise carbide to temperature of formation, say 2000° C. According to Kopp's rule the molecular heat of carbide = atomic heat of calcium + twice the atomic heat of carbon = 6.2 + 11.4 = 17.6 cal./deg. and therefore this heat = 17.6 × 2000 = ... 35,200 cal.

[1] Helfenstein in Askenasy's *Technische Elektrochemie*, **1**, p. 46, gives 1 to 10 amp./sq. cm. as the limits.

(3) The latent heat of fusion is unknown and is omitted, probably not causing much error.

(4) Assuming for carbon monoxide Le Chatelier's value of the molecular heat of permanent gases, $6.5 + 0.0006\,T$ the molecular heat = 7.8, and $7.8 \times 2000 = $ . . . . . . 15,600 cal.

Total . . . . 176,000 cal.

This corresponds to 0.220 kw.-hr. for 64 g of carbide, or 7.0 kg./24 kw.- hr. The efficiency of a furnace producing 6 kg. of 89 percent carbide per kw.-day would therefore be 5.3/7 = 76 percent.

Carbide is tapped into a cast-iron vessel about 6 in. deep which is then taken to a cooling room where the carbide is dumped on an inclined plane with rails running down the incline so that air can circulate all around the carbide. On cooling, it is broken up with hammers and is pushed down to the edge of the incline and drops on to a belt conveyor by which it is taken to the crushing and sizing plant A certain loss in carbide occurs in crushing due to the dust. This loss depends both on the kind of crusher used and the size to which the carbide is crushed. It varies from 4 percent for large sizes to 27 percent for small.

A carbide plant always provides for manufacturing the drums for packing, and usually also a plant for burning lime.[1] The cost of packed carbide at the factory varies with local conditions, but $40 per 1000 kg. may be taken as an average value.

Carborundum. — Carborundum is the name given by Acheson to crystallized silicon carbide. It was probably first produced by Despretz in connection with experiments on refractory materials, in the course of which he heated a carbon rod imbedded in sand. The sand was fused, and doubtless there was some reaction between the carbon and sand.[2] In 1886 A. H. Cowles obtained some hexagonal crystals from his furnace on attempting to melt quartz.[3] This was thought at the time to be a suboxide of silicon, but was later recognized as carborundum. In 1892 Schützenberger [4] obtained the amorphous carbide of silicon by heating silicon and carbon together. It was also made by Moissan at about the same time by several methods.[5]

In 1891 at Monongahela, Pennsylvania, E. G. Acheson [6] dis-

[1] For full description of a carbide plant, see Engineering, **87**, 405, 443, 477, 522, 546, 729 (1909).

[2] C.r. **89**, 720 (1849).

[3] Proc. Soc. Arts, 343 meeting, 1885–6, p. 74. Boston.

[4] C.r. **114**, 1089 (1892).

[5] *The Electric Furnace*, p. 274 (1904).

[6] Journ. Franklin Inst. **136**, 194 and 279 (1893).

covered the crystallized carbide of silicon, in carrying out some experiments with the object of producing crystallized carbon. The object was to dissolve carbon in melted silicate of aluminum, or clay, and by cooling to cause the carbon to crystallize. The first experiments were carried out in an iron bowl lined with carbon in which was placed a mixture of carbon and clay. The mixture was fused by means of an electric current passing between the bowl and a carbon rod directly over it. On fusion a violent reaction took place, and after cooling a few bright blue hard crystals were found. These were first supposed to be carbon, but later were taken for a compound of alumina or corundum and carbon, from which the name carborundum was made up. Subsequent to this it was found that better results were obtained when silica was used in place of clay, and when common sodium chloride was added. The reason for this was evident when the following analysis of the product was made:

	PERCENT
Silicon	62.70
Carbon	36.26
Aluminum oxide and ferric oxide	0.93
Magnesium oxide	0.11

This showed the substance in the pure state to be CSi.

The furnace in which these experiments were carried out was made of refractory bricks, the interior dimensions being 10 by 4 by 4 inches. The current was carried by a core of granulated carbon, as shown in Figure 162.
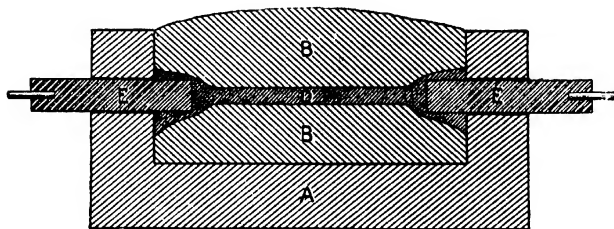
Fig. 162. — LONGITUDINAL SECTION OF ACHESON'S EXPERIMENTAL CARBORUNDUM FURNACE

Figure 163 shows an end view of this furnace and the layers of different materials after a run. B is a solid mass of sand and carbon held together by fused salt. C is chief product of the reac-

tion, crystallized carbide of silicon. W represents a white or gray-greenish-looking shell, and consists of small pieces the size of the original grains. They are soft, and may easily be reduced to fine powder, and are of no value as an abrasive, though analysis shows them to be principally carbide of silicon. It is amorphous carborundum, or *carborundum firesand*. G is graphite mixed with carborundum, and D is the core, only a portion of which becomes graphitized even though used repeatedly. The output of this small furnace was $\frac{1}{4}$ pound a day.[1]
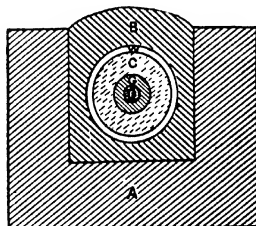
Fig. 163 — Transverse Section of Acheson's Experimental Carborundum Furnace

The furnaces used at Monongahela in 1893 were 18 inches wide, 12 inches deep, and 6 feet long. The core was of granular carbon in the form of a sheet 10 inches wide, 1 inch deep, and $5\frac{1}{2}$ feet long. In $7\frac{1}{2}$ to 8 hours a portion of the charge was transformed into 50 pounds of crystallized carborundum.

On moving to Niagara Falls the furnaces were constructed as shown in Figure 164.[2] The end walls are built of refractory brick and clay, and carry water-cooled electrodes, b^2, consisting of rectangular carbon rods clamped together. Contact is made with the copper cables by the copper plates, b^5, as shown. A are the 9-inch
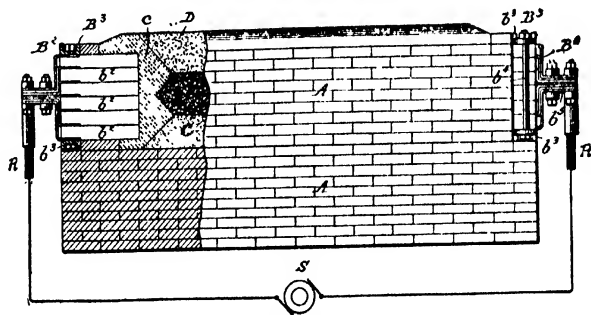
Fig. 164. — Section of Carborundum Furnace

[1] FitzGerald, Journ. Franklin Inst. **143**, 81 (1897).
[2] FitzGerald, *Carborundum*, p. 8.
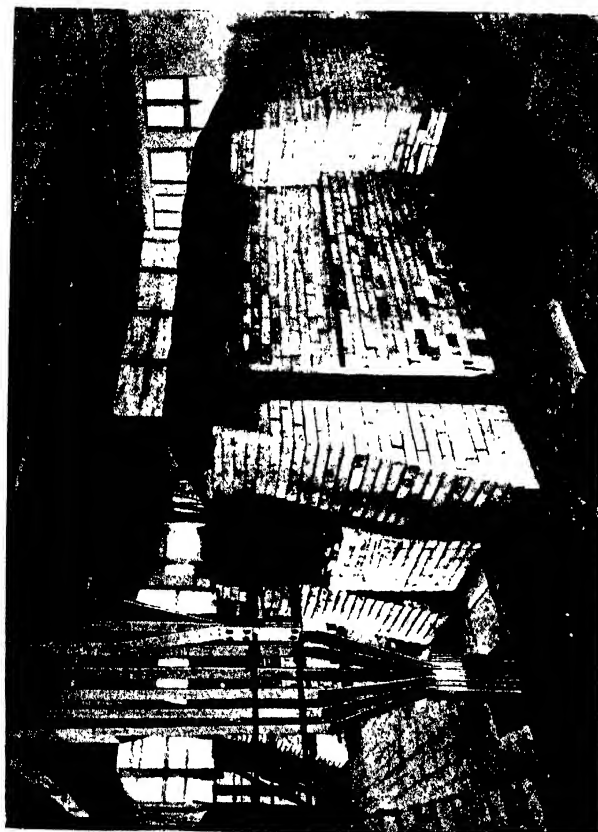
FIG. 165. — CARBORUNDUM FURNACE

Courtesy Norton Company

brick side walls of the furnace put together without cement. D is the mixture, C the core of granulated carbon, and c is fine carbon powder for the purpose of making contact between the carbon electrodes and the core. The following are the inside dimensions of a 2000-horse-power (1492 kw.) furnace : [1] 47 ft. long, 8 ft. wide, and 8 ft. high. The voltage varies between 300 and 200 volts. A perspective of the furnace in operation is shown in Figure 165.

Soon after the current is turned on, carbon monoxide is produced, due to the oxidation of the carbon in the core and in the charge. The gas is always lighted, and burns during the run. When the temperature has become sufficiently high, carborundum is formed according to the following reaction :

$$SiO_2 + 3\,C = CSi + 2\,CO.$$
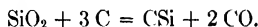
The heating lasts 36 hours, and produces 13,000 pounds of crystallized carborundum, surrounding the core to a depth of from 25 to 30 centimeters, and 4000 pounds of firesand. This corresponds to 2.6 kg. per 24 kw.-hr., while the first furnaces of the Carborundum Company at Monongahela were built for 100 kilowatts, and yielded 1.37 kg./kw.-day. A 1500-kw. furnace is known to be much more efficient than a 746-kw. furnace, but there is no information available as to whether a still larger furnace would be more efficient.

The following calculation of the efficiency of a carborundum furnace takes no account of the energy necessary to carbonize the sawdust, or to vaporize the salt, impurities, and moisture, and in making firesand. It therefore gives a lower limit for the value of the efficiency.

(1) The heat absorbed by the reaction at room temperature may be calculated by adding the following equations :

$$SiO_2 = Si + O_2 - 196,000 \text{ cal.}$$
$$Si + C = SiC + 2000 \text{ cal. [Mixter, Am. J. Sci. } \mathbf{24}, 130 \ (1907)];$$
$$\underline{2\,C + O_2 = 2\,CO + 58,320 \text{ cal.}}$$
$$SiO_2 + 3\,C = SiC + 2\,CO - 136,000 \text{ cal.}$$
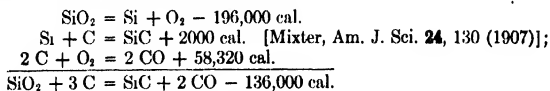
(2) The heat required to raise two mols of carbon dioxide 1500° C. is $2 \times 7.8 \times 1500 = 23,400$ cal.

(3) Assuming the atomic heat of carbon to be 5.7 and that of silicon 5.6, the atomic heat of CSi is 11.3 and the heat absorbed in heating to 2000° C. $= 22,600$ cal. Total heat for one mol (40.4 g.) $= 182,000$ cal., equivalent to 0.21 kw.-hr. One kw.-day therefore corresponds to 4.6 kg. CSi and the efficiency is $2.6/4.6 = 57$ percent.

[1] These data were supplied by Mr. O. Hutchins, of The Carborundum Company.

The raw materials used by The Carborundum Company consist of sand 99.5 percent silica, petroleum coke, sawdust, and sodium chloride. The object of the sawdust is to make the charge porous to facilitate the escape of the carbon monoxide. The core consists of graphitized coke from previous runs, decomposed silicon carbide, and new coke. Coke used in the charge is ground to 16 mesh and finer. The charge is made up in lots of 500 kilograms, and has the following composition:

Sand	261 kilograms
Coke	177 kilograms
Sawdust	53 kilograms
Salt	9 kilograms
	500 kilograms

The charge must be thoroughly mixed, as no mixing takes place in the furnace. If there happened to be an excess of silica at any part of the charge, it would react with the carbide and produce silicon according to the reaction $SiO_2 + 2 SiC = 3 Si + 2 CO$, and this occasionally happens.

There is a considerable shrinkage in the charge on account of the charring of the sawdust and the evolution of carbon monoxide.

On coming from the furnace the carborundum is ground, treated with concentrated sulfuric acid to remove impurities, washed with water, and graded.

When carborundum is heated to a sufficiently high temperature silicon is vaporized, leaving carbon in the form of graphite. The temperatures of formation and decomposition have been determined with very good agreement by three different observers.[1] The amorphous green carbide, called carborundum firesand, or siloxicon is produced in the furnace between 1600° C. and 1840° C. At 1840° C. the amorphous form changes to the crystallized, and this decomposes at 2240° C. into silicon vapor and graphite. In a vacuum carbon begins to reduce silica at 1460° C.[2]

Pure silicon carbide is colorless, but the commercial product is either green or very dark and iridescent. Iridescence is due to a thin film of silica that can be removed with hydrofluoric acid, with disappearance of colors. The impurities amount to less than 2 percent. For its chemical behavior, see under refractories.

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[1] Tucker and Lampen, J. Am. Ch. Soc. **28**, 853 (1906); Gillett, J. Phys. Ch. **15**, 213 (1911); Saunders, Tr. Am. Electroch. Soc. **21**, 425 (1912).

[2] Greenwood, J. Ch. Soc. **93**, 1492 (1908).

The principal uses of carborundum are as a refractory and as an abrasive. It is no longer used as a substitute for silicon in the steel industry. It is made into grinding wheels by mixing with kaolin and feldspar as a binder, compressing in a hydraulic press, and burning in a kiln such as is used in ceramics. Its use as an abrasive is most successful with substances of low ultimate strength, such as cast iron and brass, or substances like marble and carbon, which cannot fill the wheel. It was also used as a detector in wireless telegraphy, and in a form known as *silundum* as a resistance for heating purposes.[1] Silundum is made by exposing carbon in any finished shape to the vapor of silicon, which penetrates the carbon and changes it to carbide. This is done in the same kind of furnace as is used to make carborundum. Carbon objects are imbedded in the charge and may be entirely silicified or only covered with silundum, according to the time exposed.[2]

Silicon Oxycarbides. — There are a number of compounds of the general formula C_xSi_xO, originally discovered by Schützenberger and Colson,[3] produced according to the reaction $3\,Si + 2\,CO_2 = SiO_2 + 2\,SiCO$, which go by various names according to their origin and physical appearance. They may be called silicon oxycarbides. Acheson called his product *siloxicon*.[4] It is made in the outer region of carborundum furnaces or in specially constructed furnaces and has the composition Si_2C_2O and Si_7C_7O.

In the manufacture of carborundum firesand, as it is now called, it is important not to have sufficient carbon in the charge to reduce the silica completely, and to keep the temperature constant within certain narrow limits. For this purpose the furnace is built with more than one core, thus making the distribution of temperature more even. The charge, consisting of one third carbon and two thirds silica, is made up of powdered carbon, powdered silica, and sawdust, the silica and carbon contents of the sawdust being taken into account.

The density of carborundum firesand is 2.7.[5] When heated in an atmosphere containing a large amount of oxygen to about 1470° C., it is oxidized, giving silica and carbon dioxide,[6] while in the

[1] Bölling, Elektroch. Met. Ind. **7**, 25 (1909).

[2] For a method using SiC and an organic binder, see Hutchins, U. S. Pat. 1,266,478 (1918).

[3] C.r. **92**, 1508 (1881); **94**, 1710 (1882).

[4] U. S. Pat. 722,792, and 722,793 (1902); Electroch. Met. Ind. **1**, 287 (1903).

[5] FitzGerald, Electrochem. Met. Ind. **2**, 439 (1904).

[6] Acheson, Electrochem. Met. Ind. **1**, 373 (1903).

absence of oxygen at a higher temperature it is converted into carborundum.

Carborundum firesand is used to make crucibles and for furnace lining, as it is not attacked by melted metals or by slags.

Tone later took out a patent [1] for the same substance in fibrous form made in a carborundum furnace made by the action of vapors of silicon with carbon monoxide or dioxide. The General Electric Company makes a similar substance called *silox* or *elephant ear* by heating silicious material and carbon in a closed-arc furnace. The charge is fed into the furnace through a hopper, and the product is condensed in a separate chamber. It is a gray, porous material, is a good heat insulator, and a relatively good electric conductor. A much lighter silicon oxycarbide called *fibrox* was made by Weintraub [2] by heating silicon with calcium fluoride as catalyzer in a closed clay-lined Dixon muffle for several hours at the melting point of silicon. The muffle is then found full of this material, which has a light green color. It is the best heat insulator known, having 4200 thermal ohms per centimeter cube between 15° and 100°. Its specific electric resistance [3] is 360 ohms per centimeter cube at 25° and it has a density of only 3.7 gr./l. When wet with water it collapses and does not regain its fibrous structure on drying.

Silicon. — Silicon is made by The Carborundum Company by reducing silica rock with carbon in arc furnaces similar to that shown in Figure 160. A three-phase 3000-kilowatt furnace at 120 volts has the following dimensions: [4] 14 ft. long, 8 ft. wide, and 4 ft. deep. The walls are brick with a tar and carbon lining 6 in. thick. This furnace produces 11,000 lb. of 90 percent silicon in 24 hr. The rock is crushed to 3 in. or less, the coke to 1 in. By using high-grade silica and petroleum coke, 95 percent silicon can be made. The tappings are made every 2 to 3 hr. and weigh 2000 to 3000 lb.

Silicon can also be made from silicon carbide and silica according to the reaction $SiO_2 + 2\,CSi = 2\,CO + 3\,Si$, but this carbide must be obtained at a low price to warrant its use. Cheap silicon carbide can sometimes be obtained as a by-product from graphite furnaces. It yields high-grade silicon.

[1] U. S. Pat. 1,028,303 (1912).

[2] Tr. Am. Electroch. Soc. **27**, 267 (1915).

[3] See also Northrup, Met. Chem. Eng. **15**, 409 (1916).

[4] These data were kindly furnished by Mr. O. Hutchins, of The Carborundum Company.

The approximate efficiency of silicon furnaces can be calculated as follows :

(1) The heat absorbed by the reaction at room temperature is found by adding the equations:

$$SiO_2 = Si + O_2 - 196,000 \text{ cal.}$$
$$\underline{2 C + O_2 = 2 CO + 58,000 \text{ cal.}}$$
$$SiO_2 + 2 C = 2 CO + Si - 138,000 \text{ cal.}$$
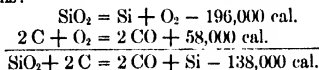
(2) The heat required to raise 28.4 g. silicon to 2000° C. is 28.4 × 0.2 × 2000 = 11,360 cal.

The heat required to raise 2 mols of carbon dioxide to 2000° = 7.1 × 2000 × 2 = 28,000 cal.

Total for 28.4 g. silicon = 177,000 cal., corresponding to 3.3 kg. per 24 kw.-hr. As the furnace produces 1.7 kg. in this time, the efficiency is 1.7/3.3 = 52 percent.

The principal uses of silicon are to make high-grade silicon steel for the electrical industry, as a reducing agent in making certain alloys of vanadium and chromium, in a new aluminum-silicon alloy used in automobiles, and for making hydrogen for balloons.

Graphite. — Graphite was known to the ancients, but up to the time of Scheele no distinction was made between it and the closely similar substance molybdenum sulfide, MoS_2.[1] Both leave a mark on paper and were called plumbago on account of the belief that they contained lead.

In order to define graphite more definitely, Berthelot [2] proposed that only that variety of carbon be given this name which, on oxidation with powerful oxidizing agents at low temperatures, gives graphitic oxide. Graphitic oxide has different properties, depending on the differences in the graphite from which it is made, but all varieties are insoluble and deflagrate on heating. Amorphous carbon, when oxidized with a mixture of potassium chlorate and fuming nitric acid, the oxidizing agent used by Berthelot, is changed to a soluble substance, and diamond is not affected. This is a method of separating the three different kinds of carbon.

The artificial production of graphite by dissolving carbon in cast iron and allowing to cool slowly was first observed by Scheele in 1778.[1] It has since been made by Moissan by dissolving in iron, as well as in a number of other metals, and by heating pure sugar carbon in the electric arc.[3] Diamond also may be changed

[1] Roscoe and Schorlemmer, *Treatise on Chemistry*, 5th ed., **1**, 751 (1920).

[2] Ann. de Chim. et de Phys. (4) **19**, 393 (1870).

[3] Moissan, *The Electric Furnace*, p. 61. See also FitzGerald, *Künstlicher Graphit*, Vol. 15 of the Engelhardt Monographien.

to graphite by heating in a vacuum to 1700° C.[1]   Despretz,[2] in his work on carbon, produced graphite by heating carbon in an electric furnace.   These observations do not agree with those of Acheson, who early in his experience in the manufacture of carborundum noticed that graphite occasionally formed next to the core [3] and that when coke from bituminous coal was used for the core quite a large amount of it was converted into graphite, whereas when the purer petroleum coke was used very little was so changed.   The greater the amount of impurity in the coke, the larger was the amount of graphite produced.   These facts led Acheson to the theory that graphite is not produced by simply heating carbon, but that a carbide must first be produced and then decomposed by a higher temperature, volatilizing the metallic element and leaving the carbon in the form of graphite.   The effect of the impurities is catalytic, since the amount of graphite formed was always too great to be accounted for by the simple decomposition of the quantity of carbide corresponding to the impurity present.   If only a small amount of impurity is present, it is lost by volatilization before all the carbon can be graphitized.   Acheson also found that the production of graphite was greatly increased by adding a considerable quantity of any substance that could form a carbide, such as silica, aluminum oxide, lime, or iron oxide.[4]   At first the charge was made up with enough impurity to change all the carbon to carbide at once.   For example, a charge would consist of 50 percent coke, with sand, salt, and sawdust.   Carborundum was then formed and by heating to a higher temperature the carborundum is decomposed, leaving graphite.   It was found, however, that so much carbide-forming element was not necessary and that such substances as anthracite coal that had impurities evenly distributed through them could be converted into very pure graphite.[5]   This is at present one of the principal kinds of carbon used in this industry.

Intimate mixture of carbon and the impurity is not necessary, as the carbide-forming element can be vaporized and caused to penetrate the entire charge, thereby converting it to graphite.[6] Petroleum coke is one form of carbon used in this process.   Lumps

[1] Thompson, Frölich, and Gillson, Tr. Am. Electroch. Soc. **43**, 161 (1923).
[2] C.r. **28**, 755; **29**, 48 and 709 (1849).
[3] Journ. Franklin Inst. **147**, 475 (1899).
[4] U. S. Pat. 568,323 (1895).
[5] U. S. Pat. 645,285 (1900).
[6] U. S. Pat. 711,031 (1902).

of the coke are imbedded in powder formed from the same material
and 5 percent of iron oxide is sprinkled in. The iron oxide is
reduced, iron is formed at the bottom of the furnace, and as the
temperature is raised volatilizes and penetrates the whole charge.
A very soft quality of graphite is obtained when the carbide-forming
material is more than 20 percent by weight of the charge, but less
than the amount necessary to change all the carbon to carbide at
once.[1]

The higher the temperature and the longer the heating the purer
is the product, as this distills the impurities and makes the graphi-
tization more complete.

Some of the experimental results on which Acheson's theory is
based were not confirmed when tested by Arsem, who finds that a
small amount of mineral matter exercises no beneficial effect in
the manufacture of graphite by heating carbon, and does not im-
prove the quality.[2] As a definition of graphite Arsem adopts the
statement that it is that allotropic form of carbon having a specific
gravity from 2.25 to 2.26. The rate of conversion to graphite is
rapid, as at 3000° C. the maximum density is reached for any form
of carbon in less than 15 minutes. Graphite is therefore the stable
form of carbon at high temperatures and is also the form most
resistant to oxidation.

The furnaces for graphitizing carbon in bulk have a central
core, as in Figure 166, to warm the furnace. When hot the charge
also carries the current.

In making graphite into electrodes, crucibles, or other finished
products, a mixture of 97 percent carbon and 3 percent iron
oxide[3] is mixed with a binding material consisting of water and
a little molasses, and is molded into the desired form. The
molded objects are then dried and placed in the furnace, where
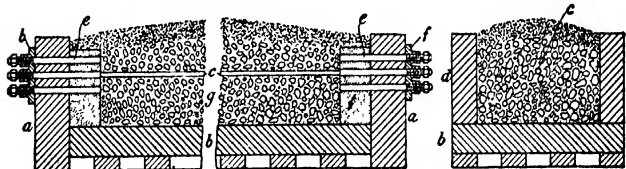
FIG. 166. — SECTION OF FURNACE FOR GRAPHITIZING CARBON IN BULK

[1] U. S. Pat. 836,355 (1906).
[2] Tr. Am. Electroch. Soc. **20**, 105 (1911).
[3] U. S. Pat. 617,979 (1899).

they are changed to graphite without altering their shape. Figures 167 and 168 show the methods of arranging rectangular and circular electrodes respectively. The base of the furnace consists of bricks, covered with a refractory material, *h*. The end walls, *b*,
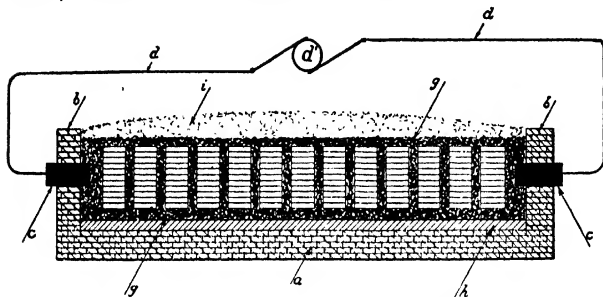
FIG. 167. — SECTION OF FURNACE FOR GRAPHITIZING RECTANGULAR ELECTRODES

are of brick and hold the carbon electrodes, *c*. The bottom of the furnace is covered with a layer of granulated coke about 5 centimeters thick, on which the electrodes are placed in piles at right angles to the axis of the furnace, separated from each other by about one fifth the width of the electrodes. This space is
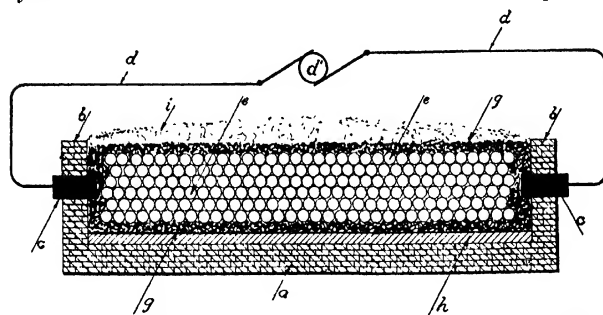
FIG. 168. — SECTION OF FURNACE FOR GRAPHITIZING CIRCULAR ELECTRODES

then filled with granulated coke, *g*, and the furnace is covered with a mixture of coke and sand, *i*. Figure 169 is from a photograph of the furnace now used for graphitizing carbon in all forms.

The following data are given by FitzGerald : [1]

Distance between terminals	360 inches
Length of space filled by electrodes	302 inches
Length of space filled by granular carbon	58 inches
Length of electrodes under treatment	24 inches
Width of electrodes under treatment	5 inches
Height of pile of electrodes	17 inches
Initial voltage	210 volts
Initial amperage	1400 amperes
Final voltage	80 volts
Final amperage	9000 amperes

As the temperature rises in a graphite furnace the following phenomena are observed : [2] (1) the volatile impurities come off and burn with a yellow flame, (2) the yellow flame is replaced by the blue flame of carbon monoxide due to the reduction of the oxides with carbide formation ; (3) the flame becomes yellow from the decomposition of carbides, with the vaporization and burning

FIG. 169. — ELECTRIC FURNACE IN WHICH GRAPHITE IS MADE ARTIFICIALLY BY THE ACHESON GRAPHITE COMPANY, NIAGARA FALLS

[1] Electroch. Met. Ind. **3**, 417 (1905).
[2] FitzGerald, *Künstlicher Graphit*, Engelhardt monographs, Vol. **15**, p. 31 (1904).

of silicon. The layer of sand and coke covering the charge is partially changed to a by-product of carborundum.

Deflocculated graphite is a form of graphite so finely divided by a special process that it will remain permanently suspended in oil or water. Mixed with water it is called waterdag, mixed with oil, it is called oildag. It is used as a lubricant.[1]

The efficiency of graphite furnaces may be calculated as follows :[2] .

In 24 hr. 746 kw. convert 5440 kg. of anthracite into 4540 kg. of graphite. This corresponds to 6.1 kg. per kw.-day.

Assume the temperature of the furnace is 3000° C., the mean specific heat of coal is 0.5, and the heat evolved on conversion 522 cal. per kg. graphite.

(1) Heat required to raise 5440 kg. coal to 3000° . . 8,160,000 kg.-cal.
(2) Heat evolved on forming graphite . . . . . . 2,370,000 "   "
Difference, or heat required from current . . . . . 5,790,000 "   "

This corresponds to 16 kg. per 24 kw.-hr. and the efficiency is therefore 6.1/16 = 37 percent. This is a lower limit on account of neglecting the heat required to vaporize the impurities. It shows, however, that the efficiency of graphite furnaces are relatively low, which would be expected from the large surface exposed.

Carbon Bisulfide. — Great improvement has been made in the manufacture of carbon bisulfide by using an electric furnace in place of the small clay or iron retorts which have to be heated externally. In the old process, only a small fraction of the heat applied to the outside of the retort penetrated to the mixture of carbon and sulfur inside, and the process was so disagreeable on account of small leaks and the high temperatures of the retort room that some manufacturers gave it up altogether. E. R. Taylor,[3] however, has succeeded in overcoming these difficulties entirely by the use of the furnace shown in cross-section in Figure 170, patented in 1899 [4] and in operation at Penn Yan, New York. This furnace is 12.5 meters high and the diameter at the base 4.87 meters.[5] At a height of 3.68 meters the diameter is reduced to 2.5 meters for a distance of 4.87 meters, where it narrows down to the top for the remaining length. The electrodes are at the base

[1] Acheson, Tr. Am. Electroch. Soc. **12**, 29 (1907).
[2] Richards, Tr. Am. Electroch. Soc. **2**, 5: (1902).
[3] E. R. Taylor, Tr. Am. Electroch. Soc. **1**, 115 (1902) and **2**, 185 (1902).
[4] U. S. Pat. 688,364, filed 1899, renewed 1901.
[5] Haber, Z. f. Elektroch. **9**, 399 (1903).

and are four in number, arranged 90 degrees apart.   Opposite electrodes are connected to the same terminal of the alternating-current machine.   Wear on the electrodes is reduced to practically nothing by covering them with conducting carbon, which acts as the resistor. Charcoal is fed in at the top and sulfur through the annular spaces in the walls, thus preventing loss of heat. The sulfur is melted by the heat which would otherwise be lost through the walls, and flows down on to the electrodes, where it is heated to a temperature at which it combines with carbon. The carbon bisulfide vaporizes, passes off through the top of the furnace, and is condensed in cooling coils. The furnace is so tight that no odor is noticeable, and its operation is continuous. The production in 1903 was 19.4 kg. per kw.-day and the furnace had been in operation for two and a half years with only one interruption for the purpose of cleaning out. In a more recent furnace differing from the Taylor furnace 20 kg. per kw.-day were obtained. It is estimated that this corresponds to 31 percent thermal efficiency.[1]

Phosphorus. — Phosphorus is another product the manufacture of which has been improved by the use of heat derived from electricity. The older method consists in treating calcium phosphate with sulfuric acid, which changes the triphosphate to monophosphate:

FIG. 170. — TAYLOR'S ELECTRIC CARBON BISULFIDE FURNACE

[1] Richter, Tr. Am. Electroch. Soc. **42**, 253 (1922).

$$Ca_3(PO_4)_2 + 2 H_2SO_4 = 2 CaSO_4 + CaH_4(PO_4)_2.$$
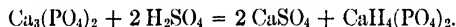
The monophosphate is then mixed with carbon and dried, by which it is changed to metaphosphate:

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2 H_2O.$$
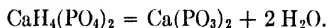
The metaphosphate is then heated in small retorts in which the following reaction takes place:

$$3 Ca(PO_3)_2 + 10 C = Ca_3(PO_4)_2 + 10 CO + 4 P.$$

This process is imperfect in that a portion of the phosphorus is changed in the last operation to the product with which the operation is begun. Wöhler proposed the use of silica and carbon, by which all the phosphorus would be recovered, as shown by the following reaction:

$$Ca_3(PO_4)_2 + 3 SiO_2 + 5 C = 3 CaSiO_3 + 5 CO + 2 P,$$
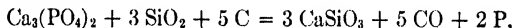
but it was never successful till the introduction of the electric furnace, on account of the difficulty of obtaining the necessary temperature and of finding vessels to withstand it.[1] Distillation begins at 1150° C. and requires 1500° for completion.[2] In 1889 the use of electric furnaces for the manufacture of phosphorus was patented by J. B. Readman.[3] The process does not seem to have been immediately employed on a large scale, however. In 1897 the firm of Albright and Wilson built works at Niagara Falls, using 300 horse power, for making phosphorus in the Readman-Parker furnace.[4] The furnaces are illustrated in Figures 171 and 172. Each produces 170 pounds a day.

Fig. 171.— VERTICAL SECTION OF PHOSPHORUS FURNACE
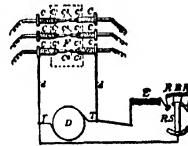
Fig. 172. — HORIZONTAL SECTION OF PHOSPHORUS FURNACE

Fused Aluminum and Magnesium Oxides. — Fused aluminum oxide, chemically identical with corundum, has received the following trade names: *alundum, aloxite, lionite, natalite, bathite, boro-carbone,* and *borolon.* The process for

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[1] Min. Ind. **14**, 494 (1905).
[2] Electrochem. Ind. **5**, 407 (1907).
[3] U. S. Pat. 147,943(1899).
[4] Min. Ind. **6**, 537(1897), **7**, 557 (1898).

making this abrasive in the electric furnace was patented in 1900 by C. B. Jacobs.[1] His furnace was rectangular in shape, made of sheet iron and brick, and was lined inside with carbon. An arc was formed between four pairs of electrodes near the movable bottom of the furnace. As the aluminum oxide fused and covered the bottom of the furnace, it was gradually lowered, thereby making a layer of fused aluminum oxide which cooled slowly. This process gives the abrasive a hardness greater than corundum.

Alundum is now made in a furnace patented by Higgins,[2] shown in Figure 173, 4 ft. in diameter by 5 ft. high, having two carbon electrodes 4 by 12 in. in cross-section, and a carbon bottom. It consists of an iron shell cooled by jets of water on the outer surface. The charge forms its own lining. The ingots weigh 2.5 tons each, and are allowed to cool several days before they are broken up.

Aloxite is made in a furnace water cooled like the above, but it is 8 ft. in diameter, with a bottom smaller than the top, while the Higgins furnace is larger at the bottom than at the top. It makes a pig weighing 4.5 tons.[3]

The charge consists of calcined bauxite mixed with sufficient carbon to reduce the impurities, the principal ones being the oxides of iron, titanium, and silicon. The reduced metals form a ferro-silicon containing 9 to 15 percent silicon and impurities of titanium, aluminum, sulfur, and phosphorus. This is heavier than the melted alumina and most of it settles to the bottom of the furnace.

Fused aluminum oxide is used principally as an abrasive and as a refractory.

Fused magnesium oxide is made in furnaces similar to those used for fusing aluminum oxide. That made by The Carborundum Company has the following composition in percent: MgO, 94.95; SiO_2, 0.60; FeO, 0.86; Al_2O_3, 2.65; CaO, 1.40.

Fused Quartz.[4] — Fused quartz is made in two forms, transparent and opaque. The opaque variety is made by Despretz's method of heating a carbon rod imbedded in quartz sand, resulting in a crude tube of fused silica. Carborundum is formed next the carbon rod, but this adheres to the carbon. These tubes are remelted and worked up into various kinds of laboratory apparatus, such as pyrometer tubes, tubes for electric furnaces, crucibles,

[1] U. S. Pat. 659,926 (1900).
[2] U. S. Pat. 856,061 (1907); Min. Ind. **19**, 28 (1910).
[3] Hutchins, U. S. Pat. 1,310,341 (1919).
[4] Berry, Tr. Am. Electroch. Soc. **45**, 511 (1924).

Fig. 173. — Fused Alundum and Alundum Furnaces

Courtesy Norton Company

etc. A crude green variety is also used for electric insulators.

During the last twenty-three years the development of clear fused quartz has made rapid progress, particularly by the Thomson Research Laboratory of the General Electric Company at Lynn. In making this variety, it is necessary to start with the highest quality of raw material; the best is water-clear crystals, containing less than 0.2 percent of impurities. These are washed in acid to remove iron oxide and other foreign material often incrusted on the surface, and are then broken up and the unsuitable pieces discarded.

These pieces are packed as densely as possible in a graphite or carbon crucible, so that during the cracking of the crystals, which occurs when the temperature is raised, the parts cannot separate and allow small amounts of gas to enter the crevices and thus give rise to bubbles. This crucible is placed in a modified vacuum furnace and the temperature is raised as quickly as possible to the melting point of about 1750° C. This usually takes 45 minutes, and 3 to 8 kw.-hr./lb. of quartz. The result of this first fusion is a clear, transparent mass, containing comparatively few bubbles, ranging in size from a pinpoint to 3 mm. in diameter. As these bubbles are formed near 1800° C. the pressure in them of any foreign gas at room temperature is very small, or if formed by silica vapor alone, it would be nothing. In order to make this into tubing, cane, or ribbon, the result of the first fusion is placed in another graphite crucible which is suspended in a vertical carbon tube furnace. A graphite piston which just fits the crucible is placed on top of the fused quartz slugs, and a weight is placed on top of a plunger attached to the piston. The quartz is then fused, the bubbles are largely collapsed, and by the action of the weight the quartz is forced out as rods, tubing, or ribbon.

When large blocks are to be made as free from bubbles as the tubing, only one fusion is carried out; this is in a vacuum furnace designed also to withstand high pressure. As soon as the quartz is fused, the vacuum valve is closed and some inert gas, such as nitrogen, is forced in to a pressure depending on the object in view. This pressure may be as high as 600 lb./sq. in., and it causes the bubbles to collapse, and gives a block freer from bubbles than many kinds of the best optical glass.

When quartz crystal is heated to between 500° and 600° C., it cracks into small pieces, sometimes with explosive violence, on account of the difference of the coefficients of expansion along the

two axes. After fusion, however, it no longer cracks on heating but can be used up to 1000° C. without injury. Its coefficient of expansion is 58×10^{-8}; a piece $\frac{5}{8}$ in. (1.6 cm.) in diameter can be heated to the melting point and plunged into ice water without fracturing. Both heat rays and ultra-violet light are readily transmitted.

Tubes, rod, ribbon, and cane can be made in lengths of 30 ft. (9.2 m.) and in shorter lengths in diameters up to eight inches. Blocks have been made up to 11.5 in. (29 cm.) in diamter and 6 in. (15.2 cm.) thick with comparatively few bubbles. Fused-quartz projection lenses 4.5 in. (11.4 cm.) in diameter have been used for months in motion-picture projection machines, where glass lenses cracked daily. Other uses that have been tested are for thermometers with no lag and for tuning forks whose rate must be independent of the temperature.

The Electrolysis of Fused Salts. — When the nature of a metal is such that it cannot be deposited from aqueous solutions on account of its reaction with water, and cannot be obtained by reduction with carbon, it is sometimes possible to produce it by electrolyzing one of its fused compounds. Aluminum, sodium, potassium, calcium, magnesium, and cerium are all made in this way. The compounds usually electrolyzed are the chlorides, oxides, or hydrates.

There are a number of practical difficulties that may occur in electrolyzing fused salts that may either cause a low efficiency or prevent entirely the production of the metal. One of these is the *anode effect.*[1] This apparently consists in a thin film of the anode gas clinging to the anode, and producing a high resistance which cuts down the current and allows the bath to freeze. It is the result of too high a current density, and the way to avoid it is to reduce the current density. Another difficulty is the tendency of some metals to remain suspended as fine globules in the fused bath, so that it is difficult to collect them. Other metals have a tendency to dissolve in the electrolyte and diffuse to the anode, where they are oxidized with a loss in current efficiency. Some metals are heavier than the bath and stay at the bottom, where they are deposited, but others float to the surface and in some cases would burn if not immediately removed. Calcium belongs to this class, while magnesium floats but does not burn. The bath itself may cause trouble by becoming pasty due to decomposition and the formation of substances with high melting points. Finally,

[1] Thompson, Electroch. Met. Ind. **7**, 19 (1909).

it is difficult to dehydrate some salts without decomposing them. If hydrated magnesium chloride is heated alone, it is completely changed to the oxide, but if previously mixed with ammonium chloride and dehydrated slowly, very little decomposition takes place, and the ammonium chloride may be subsequently removed by vaporization.

Aluminum. With the exception of silicon and oxygen, aluminum is the most widely distributed element in nature,[1] occurring principally as silicates in clays. Only a limited number of its compounds can be used for extracting aluminum, however, chief among which is bauxite, AlO_3H_3. The name *aluminum* is derived from *alumen*, a term applied by the Romans to all bodies of astringent taste.

The attempts to isolate aluminum date from 1807, when Davy was unsuccessful in applying to this problem the method employed in isolating the alkali metals. Oersted seems to have made aluminum in 1824 by heating the chloride with potassium amalgam. Wöhler in 1827 obtained aluminum by decomposing the anhydrous chloride with potassium, and in 1864 Bunsen and Deville obtained it independently by the electrolysis of fused aluminum chloride. Previous to the production by the method of electrolysis now used, the halide salts were the source of the metal and were reduced by metallic sodium.

Alumina can be reduced by carbon to metallic aluminum by heating to a temperature above 2100° C.,[2] but it is always mixed with aluminum carbide, from which it can be removed by re-melting, and obtained in a compact form. This is evidently not a method of making aluminum that could be satisfactorily carried out commercially. If, however, a metal such as copper is added to the mixture, the aluminum can be obtained as an alloy with this other metal. This process was patented in 1884 by the Cowles brothers.[3] The cheap production of pure aluminum, however, was made possible by the discovery of C. M. Hall[4] that alumina, dissolved in a melted mixture of aluminum fluoride and the fluoride of another metal, forms an electrolyte which may be decomposed by an electric current, liberating aluminum at the cathode and oxygen at the anode. Hall's original patent specifies

[1] Thorpe, *Dictionary of Applied Chemistry,* **1,** 156 (1921).
[2] Hutton and Petavel, Phil. Trans. **207,** 421 (1907); Askenasy and Lebedeff, Z. f. Elektroch. **16,** 565 (1910).
[3] U. S. Pat. 319,795 (1885). Also Proc. Soc. of Arts. 1885–1886, p. 74.
[4] U. S. Pat. 400,664 and 400,766, filed 1886.

a mixture of 169 parts by weight of aluminum fluoride and 116 parts of potassium fluoride, corresponding to the formula $K_2Al_2F_8$. The temperature of the bath is kept up to the melting point by the electrolyzing current, according to the patent of C. S. Bradley.[1] The same process was invented independently by Héroult in France at about the same time.[2]

Hall never succeeded in making his process work satisfactorily on a small scale. When he built a cell for 35 kilowatts and 2000 amperes, however, the difficulties that occurred in small-scale experiments " disappeared as if by magic. The clogging and spoiling of the bath, which had caused trouble for the past three years, did not occur on a large scale."[3] Hall therefore concludes that that is a process that works badly on a small scale and well on a large scale, but gives no explanation of this peculiarity.

Haber and Geipert[4] succeeded in making aluminum in a few runs on a small scale, though in the last run they met with irregularities. Askenasy[5] also states that if Haber's and Geipert's directions are minutely followed, the experiment never fails. This experiment is carried out a number of times every year in the electrochemical laboratory of the Massachusetts Institute of Technology, with uniform results. The anode is four round 2-inch graphite rods placed about a quarter of an inch apart, and the cell is a graphite box 6 inches square packed in crushed coke in brick walls. After this is thoroughly heated with an alternating current, it will run for an hour with 900 amperes and 12 to 14 volts and produce aluminum with a current efficiency of 60 percent. At the end of this time the anode effect always occurs, but may be removed for a few minutes by the addition of some fresh cryolite. The original electrolyte is 80 percent cryolite and 20 percent purified aluminum oxide. The trouble is not removed by adding any of the other components of the bath, such as sodium fluoride, aluminum fluoride, or aluminum oxide.

Electrolytic cells for producing aluminum consists in an iron shell with a firebrick lining inside which is a carbon lining. The cells designed for use at Whitney, North Carolina,[6] consist in iron shells 5 feet deep, 12 feet long, and 9 feet wide. After the lining

[1] U. S. Pat. 464,933 (1891); 468,148 (1892); 473,866 (1892).
[2] U. S. Pat. 387,876 (1888).
[3] Hall, Met. Chem. Eng. **9**, 71 (1911).
[4] Z. f. Elektroch. **8**, 1 and 26 (1902).
[5] *Technische Elektrochemie*, **2**, 278 (1916).
[6] Min. Ind. **23**, 18 (1914); **27**, 20 (1918).

is put in, the cavity is 7 inches by 4 feet by 8 feet. The current is 20,000 amperes at 7 volts. One cell is expected to produce 135 kg. of aluminum a day, which would correspond to 83 percent current efficiency. The energy yield is usually 0.7 kg. per 24 kw.-hr. The aluminum is tapped from time to time.

The temperature of the bath is in the neighborhood of 1000° C., which is the melting point of cryolite.

The anodes are graphite made from petroleum coke. From 0.7 to 0.9 kg. of anode is consumed for a kilogram of aluminum. The oxygen liberated on the anodes burns them to varying proportions of carbon monoxide and dioxide, depending on the temperature. This is shown in Table 53.[1]

TABLE 53. COMPOSITION OF GAS FROM ALUMINUM ELECTROLYTIC BATHS

	PERCENT BY VOLUME	
	At 945° C	At 1055° C.
Carbon dioxide	45.6	6.0
Carbon monoxide	43.6	86.4
Oxygen	0.8	1.2
Nitrogen	10.	6.4

As the lower temperature favors the production of carbon dioxide, it would use up less anode material. Whether it would also save voltage depends on whether the concentration of oxygen at the anode is less when dioxide is formed rather than monoxide. It would be natural to expect less oxygen the higher the temperature and consequently a lower polarization electromotive force.

The following is an estimate of the cost of the different items required to make a pound of aluminum:[2]

	CENTS
16 kw.-hr. at 0.14¢	2.24
2 lb. alumina at 2.27¢	4.54
0.8 lb. anode at 3.18¢	2.54
0.12 lb. cryolite at 3.64¢	0.44
0.05 lb. aluminum fluoride at 4.54¢	0.27
0.15 working hours at 5.12¢	1.38
Miscellaneous	1.38
Total	12.79

The only producer of aluminum in the United States is the Aluminum Company of America, having works at Massina, New

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[1] Seligman, Min. Ind. **25**, 40 (1916).
[2] Min. Ind. **27**, 20 (1918).

York; Maryville, Tennessee; Badin, North Carolina; Niagara Falls, and Shawinigan Falls, P. Q.

The raw material is bauxite from Arkansas, which is converted to alumina by the Bayer process. This consists in calcining the bauxite to remove water and organic material. It is then finely ground and treated with caustic soda of specific gravity 1.45 for several hours under high steam pressure. Aluminum dissolves as $NaAlO_2$ and is filtered. This solution is treated for 36 hours with aluminum hydrate, precipitating 70 percent of the dissolved alumina. This is calcined at $1100°$ to $1200°$ C. and is then ready for use.[1]

Other sources than bauxite have not yet been used in the aluminum industry.[2]

The uses[3] of aluminum have increased enormously during recent years, and it is now the fourth non-ferrous metal as regards quantity produced, the order being copper, zinc, lead, aluminum. As a powder it is used in the Goldschmidt process, as a paint, and for explosive mixtures. A mixture of aluminum powder and ammonium nitrate is called *ammonal*, and is used in mining and in high explosive shells. The reaction is $3 NH_4NO_3 + 2 Al = Al_2O_3 + 6 H_2O + 3 N_2$. Aluminum is used as a deoxidizer in the steel industry in the form of lumps.

Aluminum cables are used in thirty long-distance transmission lines in North America. These cables consist of aluminum wire twisted over a galvanized steel core. For equal conductivity they weigh 80 percent of copper conductors and are 57 percent stronger. They consequently require fewer towers and insulators, and have less leakage and a lower cost of erection.

A number of aluminum alloys are used in automobile and airplane construction. *Magnalium* consists of aluminum containing up to 6 percent of magnesium. *Duralumin* contains 0.5 percent magnesium, 0.5 to 0.8 percent manganese, and 3.5 to 4.5 percent copper. An alloy of aluminum and silicon is used in automobiles.

Calorizing[4] consists in heating metals with aluminum powder in revolving drums, in an atmosphere of hydrogen. This alloys the surface with aluminum and makes it resistant to oxidation and corrosion.

[1] Thorpe's *Dictionary of Applied Chemistry*, **1**, 160 (1921).

[2] For an account of other possible sources of aluminum see Bureau of Mines Bull. 77, p. 78 (1916).

[3] Keeney, The El. Journ. **17**, 206 (1920); Min. Ind. **24**, 17 (1915); Min. Ind. **23**, 21 (1914).

[4] Min. Ind. **23**, 21 (1914).

The use of aluminum for kitchen ware and for innumerable small objects for personal use is too well known to require further mention.

Sodium and Potassium. — Sodium and potassium were first isolated by Davy [1] by electrolyzing the corresponding fused hydrates. In this process sodium is liberated at the cathode while the negatively charged hydroxyl ion is liberated at the anode. Two of these ions when discharged react together according to the reaction :

$$2\,OH = H_2O + O.$$
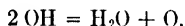
A certain amount of metallic sodium dissolves in the hydrate, diffuses to the anode, and coming in contact with the water reacts to form hydrate with the liberation of hydrogen.[2] It is therefore possible to have both hydrogen and oxygen evolved at the anode, resulting in explosions. At the same time sodium peroxide (Na_2O_2) is formed. The water formed at the anode is not driven off by the temperature of the bath ; on the contrary it has been found that very moist air is dried to a certain extent in passing through the melted hydrate.[2]

The apparatus nearly universally used for the production of sodium and potassium is due to Hamilton Young Castner [3] and is shown in Figure 174. It consists in a cast-iron box with an iron cathode, H, insulated from the box and held in an iron pipe fastened into the bottom of the cell. The space between the pipe and electrode is filled with melted hydrate which is allowed to solidify before the electrolysis is begun. Surrounding the cathode is a fine iron-gauze diaphragm, M, outside of which is the iron anode, F. The metal is liberated on the cathode and floats to the surface of the hydrate, where it collects in an iron cylinder forming a continuation of the diaphragm. It is removed by an iron spoon with fine perforations, which allow the hydrate to drain off, but which holds the metal. The hydrate is added as it is used up, and the process is continuous. An important point is to maintain the temperature as low as possible, not over 20° above the melting point of the hydrate. The higher the temperature the less the yield in metal, due of course to its greater solubility in the melted hydrate. As the temperature increases, the yield becomes less, until

[1] Phil. Trans., 1808, pp 5 and 21. See also a review by Batsford, Chem. Met. Eng. **26**, 888 and 932 (1922).
[2] Lorenz, *Elektrolyse Geschmolzener Salze*, **I**, 25 (1905).
[3] U. S. Pat. 452,030, filed 1890.
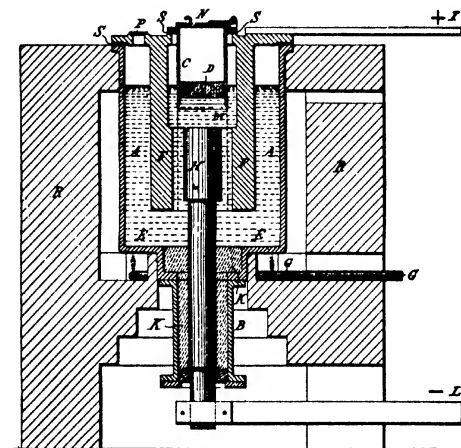
Fig. 174. — Section of Castner Cell for Producing Sodium and Potassium

it finally reaches zero. At best the current efficiency is said to be only about 45 percent.[1] In the patent gas heating is provided, though it is stated that the current can be so regulated as to keep the proper temperature without external heating.

There are other processes very similar to that of Castner, some of which are in use,[2] which will be omitted as presenting no new principles; but the principle of the following process, due to Ashcroft, will be described because of its novelty and in spite of the fact that it does not seem as yet to have been carried out on a commercial scale. Melted sodium chloride is electrolyzed with a lead cathode. The lead-sodium alloy formed is let into another cell containing melted sodium hydrate. Here the lead alloy acts as the anode and forms sodium hydrate with the hydroxyl ions liberated on its surface, thus avoiding the formation of water and oxygen. At the cathode sodium is liberated and removed. To decompose the chloride 7 volts are required, and 2 volts for the hydrate when this anode is used. The voltage is therefore about twice that required in the Castner cell; but as the current efficiency is about 90 percent, or twice that in the Castner process, the yield

[1] Ashcroft, Tr. Am. Electroch. Soc. **9**, 123 (1906).
[2] See H. Becker, *Die Elektrometallurgie der Alkalimetalle*, p. 52 (1903), Vol. 15 of the Engelhardt Monographs.

per unit of power is the same in the two cases. The advantages claimed by Ashcroft are shown in the following table:

	ASHCROFT PROCESS	CASTNER PROCESS
Cost of material	0.5 cent per pound	5 cents per pound
Cost of power per pound of sodium . .	1 to 5 cents	1 to 5 cents
Labor	1 cent	2½ cents
Upkeep and standing charges	2.5 cents	2 cents
Total	5 to 9 cents per pound	10 to 14 cents per pound

The saving comes in the greater cheapness of the raw material, and there would be a further saving in the value of the chlorine produced.

A large part of the sodium made is consumed in the manufacture of sodium cyanide and sodium peroxide. The process for cyanide [1] consists in passing ammonia over the metal heated in an iron retort to 300° to 400° C., forming sodamide:

$$2 Na + 2 NH_3 = 2 NaNH_2 + H_2.$$
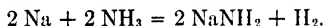
This is then treated with charcoal previously heated to redness, giving the cyanide:

$$NaNH_2 + C = NaCN + H_2.$$
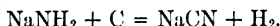
A recent purpose to which the metal has been put is the drying of transformer oils. Ashcroft believes a reduction in the price may increase its uses materially, such as making primary cells, obtaining hydrogen by the decomposition of water, and even for transmitting electric power. The specific conductivity is only about one third that of copper, but if equal weights of metal are considered between two given points, the conductivity would be three times that of copper, as the density of copper is about nine times that of sodium. Some experiments have actually been carried out in power transmission with the sodium protected in iron pipes.[2]

At one time the Acker process [3] was in operation at Niagara Falls for making anhydrous sodium hydrate directly from sodium

[1] Roscoe and Schorlemmer, *Treatise on Chemistry*, **2**, 276 (1907).
[2] Betts, Min. Ind. **15**, 688 (1906) and El. World, **48**, 914 (1906).
[3] Tr. Am. Electroch. Soc. **1**, 168 (1902).

chloride. Melted sodium chloride was electrolyzed on a lead cathode and the resulting alloy was treated with a jet of superheated steam, converting the sodium to hydrate, which floated on the lead. After its removal the lead circulated back to the electrolyzing chamber. The difficulties of keeping this process in operation were too great to make it profitable.

Calcium. — Calcium was first isolated by Davy in 1808.[1] Lime was mixed with red oxide of mercury, slightly moistened and placed on a piece of platinum. A globule of mercury in a cavity at the top acted as cathode, giving on electrolysis an amalgam of calcium, from which the mercury was distilled.

Bunsen[2] obtained calcium in very small quantities containing a little mercury by electrolyzing with a high current density a boiling concentrated solution of calcium chloride acidified with hydrochloric acid. The cathode was amalgamated platinum wire. Rathenau[3] was first to obtain calcium in a compact form in fairly large quantities by a rather original method. The bath consists of calcium chloride very little above its melting point. An iron rod is used as cathode, which just touches the surface of the bath. As the melting point of calcium is a little higher than that of the bath, it solidifies on depositing and adheres to the rod, which is gradually raised, thus drawing out a stick of calcium with a certain amount of chloride adhering to it. It is not necessary to lower the melting point of the electrolyte by adding calcium fluoride.

A suitable laboratory cell for this electrolysis can be made by lining a sheet-iron box with firebrick. Two graphite anodes are placed at opposite sides covering the whole area of these sides. This large anode area prevents the anode effect, which would otherwise be very troublesome. The calcium in contact with the cathode must be liquid, otherwise the rod drawn out will contain calcium chloride. In order to accomplish this, it must be possible to regulate the voltage across the cell constantly in order to regulate the temperature. This is done by varying the exciting current of the generator. It takes some experience to carry out this electrolysis successfully. The chloride can be dehydrated and melted in the electrolysis cell by playing a large blastlamp flame on the chloride; it does not hydrolyze. It should be melted down in thin layers and each layer should be allowed to solidify before adding more chloride, otherwise there is danger of explosions.

[1] Alembic Club Reprints, No. 6, p. 48, Ostwald Klassiker, No. 45.
[2] Pogg. Ann. **91**, 623 (1854), in an article on the preparation of chromium.
[3] Z. f. Elektroch. **10**, 508 (1904).

This electrolysis can be carried out by withdrawing the cathode, at a regular rate by a motor.[1]

A cell, shown in Figure 175, with a submerged cathode has been patented by Seward and von Kügelgen.[2] This cell consists of a circular iron box, A, through the bottom of which projects a conical iron cathode, B, insulated from the box by insulating material, aa. The anode, C, is a carbon lining also insulated from the iron box. Above the cathode and concentric with it is a water-cooled collecting ring, E, which separates the metal rising to the surface from the chlorine. The metal accumulates till the ring is full.

FIG. 175. — SECTION OF CELL OF SEWARD AND VON KÜGELGEN FOR THE PRODUCTION OF CALCIUM

The top layer is solid, due to the cooling of the air, and the bottom is soft or melted. The solid part is fastened to a hook, F, and gradually drawn out.

Calcium metal has very little use in the pure state, but when alloyed with lead it makes a good bearing metal. When used for this purpose the alloy can be made by electrolyzing calcium into

[1] Brace, Tr. Am. Electroch. Soc. **37**, 465 (1920); Chem. Met. Eng. **25**, 105 (1921).

[2] U. S. Pat. 880,760 (1908); Min. Ind. **17**, 99 (1908); **16**, 131 (1907).

a melted-lead cathode. *Frary metal*, consisting of lead containing 2 percent of calcium and barium, is made by the United Lead Company at Keokuk, Iowa, by electrolyzing mixtures of calcium and barium chlorides, in iron pots with lead cathodes.[1] Apparently this electrolysis does not go as smoothly as the straight calcium electrolysis, as it is said there is a tendency to arcing, fogging, and the production of carbides. At the end of three days' continuous electrolysis the cathodes contain 2 percent of the alkaline earth metals.

Magnesium. — Magnesium was first prepared in an impure state by Davy [2] by reducing its oxide at white heat with potassium vapor. Bunsen[3] was the first to produce magnesium by the electrolysis of fused magnesium chloride. This is the present method of its manufacture.

It is difficult to remove the water of crystallization of magnesium chloride without changing it to the oxide. Several methods have been proposed to overcome this difficulty. Bussy [4] made the anhydrous chloride by heating a mixture of magnesia and carbon in chlorine; Liebig [5] dehydrated after mixing with ammonium chloride; Matthiessen proposed the use of carnallite ($MgCl_2 \cdot KCl \cdot 6 H_2O$) whose principal source is the mines at Stassfurt. Several schemes for avoiding the use of chloride altogether have been patented by Seward and von Kügelgen, one of which is modeled on the aluminum electrolysis. Magnesia is dissolved in magnesium fluoride or in a mixture of magnesium fluoride and a fluoride of some alkaline or alkaline-earth metal. A mixture which is said to give good results consists of two parts of magnesium fluoride, one part of lithium fluoride, and one part of calcium fluoride.[6] According to Tucker and Jouard, the electrolysis of a bath of this kind gives no metal,[7] but it is being developed by the American Magnesium Corporation at Niagara Falls.

In the electrolysis the metal has a tendency to deposit on the cathode in small globules which do not easily unite. According to Oettel this is due to a thin film of oxide caused by an impurity of magnesium sulfate, which gives oxide according to the reaction

[1] Cowan, Simpkins, and Hiers, Tr. Am. Electroch. Soc. **40**, 27 (1921).
[2] Phil. Trans. **98**, 336 (1808).
[3] Liebig's Ann. **82**, 137 (1852).
[4] Journ. de Chim. medicale **6**, 141 (1830).
[5] Pogg. Ann. **19**, 137 (1830).
[6] Electroch. Met. Ind. **6**, 160 (1908); U. S. Pat. 880,489 (1908).
[7] Tr. Am. Electroch. Soc. **17**, 249 (1910); see, however, *Magnesium*, American Magnesium Corporation, p. 4 (1923).

$MgSO_4 + Mg = 2 MgO + SO_2$.[1] Natural carnallite should therefore have the impurities removed before electrolyzing, or should have them made harmless by the addition of enough sodium chloride to make the composition correspond to the formula $MgCl_2 \cdot KCl \cdot NaCl$ as patented by the Magnesium Gesellschaft at Hemelingen.[2] The presence of some calcium fluoride helps in causing the globules to unite, possibly by dissolving the oxide film.

Bunsen's cell for magnesium was divided into anode and cathode compartments by a non-conducting diaphragm which did not reach to the bottom of the cell. The salt was kept fused by the current.

In Borchers' experiments with carnallite the current density on the cathode was 10 amp./sq. cm. (93 amp./sq. ft.) with 7 to 8 volts applied. The temperature was not much above the melting point of magnesium (650° C.) because at this temperature the metal is heavier than the fused salt and sinks to the bottom, while at bright red heat the metal floats to the surface.

Bunsen produced magnesium with a current efficiency of 59.8 percent, using fused magnesium chloride, whose melting point is 711° C.[3] Oettel used carnallite and reached a current efficiency of 90 to 95 percent, while Tucker and Jouard did not exceed 60 percent. In all these experiments, the magnesium had to be remelted to get it into large pieces.

Magnesium can also be made by drawing it out of the bath on the cathode as is done with calcium,[4] but as magnesium does not burn in floating on the bath there does not seem to be any reason for using this method.

The Haag cell [5] formerly used in Germany has three compartments. In the first the salt is fused by a resistance furnace; from here it flows into the second chamber, where electrolysis takes place. The third compartment receives the magnesium and carnallite, where the two are separated.

The large demand for magnesium during the war caused several companies in this country to start its manufacture. Among these was the General Electric Company, which operated according to patents taken out by Dantsizen and Wallace.[6] Magnesium

[1] Z. f Elektroch. **2**, 394 (1895).

[2] Borchers, *Electric Smelting and Refining*, p. 16 (1904).

[3] Lorenz, *Elektrolyse geschmolzener Salze*, **2**, 7 (1905).

[4] Arndt and Kurze, Z. f. Elektroch. **18**, 994 (1912).

[5] Kershaw, *Electrometallurgy*, p. 223 (1912).

[6] Anhydrous magnesium chloride, U. S. Pat. 1,276,499; electrolysis cell, U. S. Pat. 1,190,122 (1916).

chloride is mixed in solution in equi-molecular proportions with ammonium chloride and is dehydrated at a temperature between 215° and 230° C., requiring about 8 hours. After dehydration the mixture is charged into a fused bath of magnesium chloride at 500° to 600° C. The ammonium chloride is volatilized and is collected in a condensing chamber. The electrolyzing chamber consists of an iron box lined with magnesite brick 22 in. long, 18 in. wide, and 14 in. deep. The cathode is a submerged iron rod midway between two graphite anodes placed at the sides of the cavity next the lining. The metal floats to the surface and is ladled out without any appreciable oxidation. The current efficiency is between 50 and 75 percent. The cells take 10 to 15 volts each, and 1800 amperes.

In order to avoid the danger of short-circuiting the cell by the floating magnesium or to prevent its loss by recombination with chlorine at the anode, the Magnesium Company of Wolverhampton, England, first electrolyze with a lead cathode and then use the lead-magnesium alloy as anode in another cell.[1] Both cells are made of cast steel lined with brick. They are in series and take 500 amp., the first at 5 volts, the second at 2. The cathode current density in the first cell is 1500 amp./sq. ft. In the second cell the cathodes are a large number of small-diameter steel rods, and the magnesium is removed as it is produced. In the first cell the current efficiency is 85 percent, and the total energy efficiency of the process is 40 percent, corresponding to 1.28 kg./kw.-day. In this process the chloride is dried first in a current of air at 150° C. for several hours with the removal of half of the water of crystallization, and it is then treated with hydrochloric acid at 300°. Sodium chloride or potassium chloride is added to lower the melting point from 750° C.

The uses of magnesium are principally for illumination in photography and signaling, and as a deoxidizer in the steel and nickel industry.[2] Several light and strong alloys are made from magnesium. Magnesium containing 2 to 4 percent zinc is said to be better than aluminum-magnesium alloys. It has a specific gravity of only 1.8.

Cerium. — Cerium, or a mixture of cerium with other rare-earth metals, can be made by electrolyzing the corresponding chlorides if the proper conditions are maintained.[3] An iron pot as cathode

[1] S. T. Allen, Chem. Met. Eng. **26**, 987 (1922).
[2] Min. Ind. **7**, 498 (1898); **17**, 631 (1908); **19**, 467 (1910).
[3] Thompson, Met. Chem. Eng. **17**, 213 (1917); Hirsch, Tr. Am. Electroch. Soc. **20**, 1 (1911); **37**, 359 (1920).

containing the fused chlorides and graphite anode, suitably supported, are all the apparatus required. There is no necessity for the complicated cell described by Muthmann, Hofer, and Weiss.[1]

The raw material, cerium dioxide, is a by-product of the Welsbach mantle industry. Some samples of the dioxide dissolve readily in hydrochloric acid with the evolution of chlorine, according to the reaction $CeO_2 + 4\,HCl = CeCl_3 + 2\,H_2O + \frac{1}{2}\,Cl_2$, and others do not. An insoluble sample may be changed to the chloride by first making cerium carbide by reduction with carbon and then treating this with hydrochloric acid. The chloride solution can be evaporated to dryness and melted without serious decomposition by heating in an iron pot over a blastlamp. The small amount of oxide formed on evaporation is converted back to chloride by the chlorine evolved by the electrolysis.

On electrolyzing the fused chloride, cerium collects in a solid lump at the bottom of the iron vessel, which usually has to be broken to remove the metal. The voltage, temperature, and distance apart of the electrodes have to be properly adjusted to make this electrolysis succeed. Too high a current makes the temperature too high and causes the bath to swell up like a sponge and turn black. If the current is reduced to the proper value, the bath can be regenerated by the chlorine produced. The current efficiency varies from 13 to 35 percent.

The uses of cerium are to make the pyrophoric iron alloy containing 30 percent iron which is used in gas lighters, and it is also used to deoxidize cast iron.[2]

Zinc. — The extraction of zinc by electrolyzing fused zinc chloride has been attempted on a semi-commercial scale,[3] in the Swinburne-Ashcroft process and in the Malm process,[4] but as further development has ceased, this process will not be described.

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[1] Liebig's Ann. **320**, 231 (1902); **331**, 1 (1904).
[2] Moldenke, Iron Age, **105**, 324 (1920).
[3] Electroch. Met. Ind. **3**, 65 (1905).
[4] Eng. and Min. Journ. **101**, 679 and 864 (1916).

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CHAPTER XIX

THE ELECTROTHERMIC REDUCTION OF METALLIC OXIDES, STEEL REFINING, AND BRASS MELTING

General Discussion. — Before giving an account of the application of electric heating to the iron and steel industry, a short sketch of the older methods of extracting and refining iron will not be out of place.

The extraction of iron from its ores, consisting principally of oxides of iron mixed with clay, silica, and other impurities, is
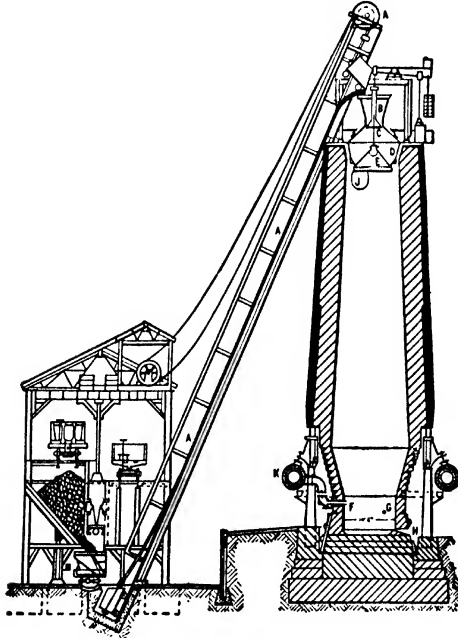
FIG. 176. — SECTION OF BLAST FURNACE

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accomplished by reducing the ore with some form of carbon, usually coke. This operation is carried out in a blast furnace, a circular brick structure lined with silicious brick, and varying in size from 48 feet to 106 feet in height, and from 8 feet to 15 feet in diameter at the base. Figure 176 shows the elevation of a blast furnace. It consists of three principal parts: (1) the crucible or hearth at the base, cylindrical in shape, (2) the bosh directly above, which gradually widens, and (3) the stack, from which point the furnace contracts for the rest of its height. The furnace is filled with alternate layers of ore, coke, and flux, the latter usually consisting of calcium carbonate. The object of the flux is to form a fusible slag with the constituents of the ore which are not reduced by the carbon, such as silica and alumina. The heat necessary to raise the charge to a temperature high enough for reduction is produced by the combustion of the coke in the charge, by means of air forced in through the tuyères, F, projecting through the wall of the furnace just below the bosh. The carbon therefore serves the double purpose of furnishing the heat and of reducing the ore.

The highest temperature of the furnace is near the tuyères and a few feet above them; in this region the slag and iron melt and drop into the crucible, where they separate, the slag floating on the iron. These are drawn off from time to time through the tap-holes G and H, and fresh material is fed into the top of the furnace by mechanical means. The iron thus produced is known as pig iron, and contains from 3 to 4 percent of carbon, as much as four percent of silicon, and 1 percent of manganese, and a few hundredths of 1 percent of sulfur and phosphorus. Only about 25 percent of the pig iron made in this country is used without subsequent purification.[1] Purification or refining of iron is accomplished by oxidizing the impurities and causing them to form a slag, which floats on the iron.

One method of refining consists in blowing air through the liquid metal in a Bessemer converter. The lining of the converter may be either basic, consisting of calcined dolomite (calcium and magnesium oxides), or acid, consisting of silica. The Bessemer method is very rapid, silicon and manganese oxidizing in about four minutes from the time when the air is first blown in. The carbon then begins to oxidize to carbon monoxide, which boils up through the metal and comes out of the converter in a long flame. In about six minutes from the time the carbon

[1] Stoughton, *The Metallurgy of Iron and Steel*, 3d ed., p. 48 (1923).

begins to oxidize, it is reduced to approximately 0.04 percent, and the operation is then stopped. The temperature is higher at the end of the process than at the start, due to the heat of oxidation of the impurities. A calculated amount of carbon is then added, also 1.5 percent of manganese to remove the oxygen, and 0.2 percent silicon to remove the other gases. The steel is then cast into molds.

The second method is known as the basic open hearth or Siemens-Martin process. The charge consisting of about 55 percent steel scrap and 45 percent cast iron is refined in a large reverberatory furnace. The cast iron is added in the liquid state when the scrap is beginning to melt. The slag consists in limestone, and heavy black magnetite is added to oxidize the impurities. This is assisted by the excess of oxygen in the furnace gases. A longer time is required to remove the impurities than in the Bessemer process, and it is therefore never used for cast iron alone.

The third method of purification is known as the puddling process, in which the iron is melted on the hearth of a reverberatory furnace lined with oxides of iron. The pig iron is charged by hand through the doors of the furnace and is melted as quickly as possible. During melting, silicon and manganese go into the slag, as well as some of the oxide of the lining. Iron oxide is then added in order to make a very basic slag; the charge is thoroughly mixed, and the temperature is lowered to the point where the slag begins to oxidize the phosphorus and sulfur before the carbon. After the removal of these impurities, the carbon begins to oxidize and comes off as carbon monoxide, which burns on coming in contact with the air. During this time the puddler stirs the charge vigorously with a long iron rabble, an instrument shaped like a hoe. As the iron becomes pure, its melting point rises and it begins to solidify, since the temperature of the furnace is below the melting point of pure iron. The iron is finally removed in the form of a ball dripping with slag, and is put through a squeezer to remove the slag as much as possible. This product is known as *wrought iron*. It is converted into steel by two methods, (1) the cementation, and (2) the crucible process. In the cementation process the wrought iron is carburized by heating, without melting, in contact with carbon. The carbon slowly penetrates the iron and changes it to steel. In the crucible process the wrought iron is cut up into small pieces and is melted in covered crucibles with the desired amount of carbon or other element that is to be alloyed with it. When the process is finished the steel is cast into molds.

By thus remelting the iron, the slag is removed and the required amounts of carbon, silicon, and manganese are added.

The Electrothermic Reduction of Iron Ores. — The conditions under which electric heating can economically be substituted for the heat of combustion of coke in the reduction of iron ores are purely local. In places where iron ore can be obtained cheaply, where metallurgical coke is expensive, where water power is cheap, and where iron would have to be hauled from a great distance to supply the local demand, it may be possible to produce iron by electric heating at a price low enough to compete with that brought from a distance.[1]

In the blast furnace the reduction of iron ore is effected by the carbon monoxide from the combustion of carbon, according to the reaction $Fe_2O_3 + 6\ CO = 2\ Fe + 3\ CO + 3\ CO_2$.[2] More carbon than the theoretical amount is required, because 3 percent of the weight of pig iron is carbon which comes from the charge, and another amount is used in reducing the impurities. About one ton of fuel is required for a ton of pig iron.

In an electrically heated furnace the reaction is $Fe_2O_3 + 2\ C = 2\ Fe + CO + CO_2$, consequently only one third as much carbon is required as in the blast furnace.

The calculated yield of iron containing 3 percent of carbon, 1 percent of silicon, 96 percent of iron, and traces of manganese, phosphorus, and sulfur, made from a charge containing 60 percent of iron in the form of magnetite, is 5.9 tons per kilowatt-year,[3] while about 3.9 tons is attained in practice. Therefore, if the cost of pig iron depended only on the cost of coke and electric power, the cost of production by the blast furnace and by the electric furnace would be equal when the cost of one ton of coke equals the sum of the costs of one third of a ton of coke plus one fourth of a kilowatt-year, or when the cost of one kilowatt-year equals that of $2\frac{2}{3}$ tons of coke.

The first attempt to apply electric heating to the metallurgy of iron was made in 1853 by Pinchon,[4] and in 1862 Monkton took a patent in England for the reduction of ores by the electric current. Sir William Siemens again called attention to this subject in a lecture before the Society of Telegraph Engineers in London

[1] Eugene Haanel, Tr. Am. Electroch. Soc. **15**, 25 (1909), and P. McN. Bennie, *ibid.*, p. 35.

[2] Richards, *Metallurgical Calculations*, p. 278 (1918).

[3] Presumably long tons, 2240 lb. or 1000 kg. Lyon and Keeney, *Electric Furnaces for Making Iron and Steel*, Bureau of Mines Bull. **67**, p. 30 (1916).

[4] B. Neumann, *Electrometallurgie des Eisens*, p. 3 (1907).

in 1880.[1] The first, however, to show by experiments on a large scale that iron can be reduced commercially by electric heating was the Italian army officer, Major Stassano.[2] Patents were taken out by him in the year 1898 in different countries, consequently this date marks the beginning of the actual application of electricity to the metallurgy of iron. The contraction of the carbide industry in 1899 to 1900, due to overproduction, leaving idle a number of water-power stations in southeastern France, for which some new application of electric power was needed, also hastened the introduction of electric heating in the iron industry.[3]

Stassano's preliminary experiments on the reduction of iron ore were carried out at Rome in 1898,[4] with the 150-horse-power furnace represented in Figure 177. It is seen to resemble an ordinary blast furnace. Since there was no combustion of carbon, no reducing gases were produced; consequently, in order to bring the carbon and ore in intimate contact, they were powdered, mixed, and made into briquettes with pitch as a binder. The furnace was first heated without a charge; an iron grating was then placed in the furnace 20 centimeters
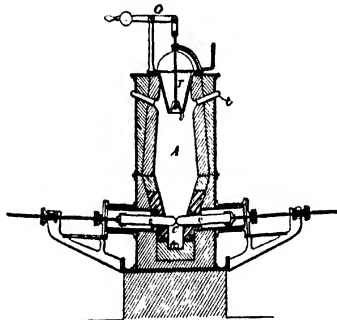
Fig. 177. — Section of Stassano's First Furnace at Rome

above the arc, and the mixture was charged in from the hopper at the top and was held up by the grating. The grating eventually melted, and the ore in contact with it was reduced. In this state the mixture which lay on the grating became fused and formed an arch, which supported the charge even when the grating melted away. As the heat from the arc penetrated the mass above the arch, iron was reduced and dropped into the crucible below. In the course of twelve hours the arch increased so in thickness, due to the slag produced, that it prevented the efficient heating of the charge above. Consequently this form of furnace was given up, and one

[1] Elektrotech. Z. 1, 325 (1880).
[2] Askenasy, *Technische Elektrochemie*, 1, 94 (1910).
[3] J. B. C. Kershaw, *Electrometallurgy*, p. 175 (1908).
[4] See an article by Stassano reprinted in Haanel's Report, p. 178 (1904).

was adopted in which the material was introduced below the arc as is done in refining furnaces. The final form adopted at Darfc in northern Italy, i shown in Figures 178 and 179. Movement of the entire chamber in which the fusion takes place is effected by rotating about an axis inclined to the vertical. The electricity is conducted to the furnace by sliding contacts on two metal rings at the top of the furnace. This furnace worked perfectly satisfactorily, even when run for several days. The most difficult questions to decide were the relation between the size of the cavity and the energy to be supplied, and the manner of making the

Fig. 178. — HORIZONTAL SECTION OF THE STASSANO FURNACE

refractory lining. The carbon electrodes were 1.5 meters long and lasted sixty consecutive hours. The furnace was supplied with 1000 amperes at 100 volts, and since the value of the cosine of the phase difference between electromotive force and current was 0.8, the power consumed was 80 kilowatts. The best yield with this furnace was one kilogram of soft iron for 3.2 kilowatt-hours, and the iron obtained was always over 99 percent pure. The ore, which was from the island of Elba, had the following composition:

	PERCENT
Fe_2O_3	93.020
MnO	0.619
SiO_2	3.792
CaO, MgO	0.500
Sulfur	0.058
Phosphorus	0.056
Moisture	1.720
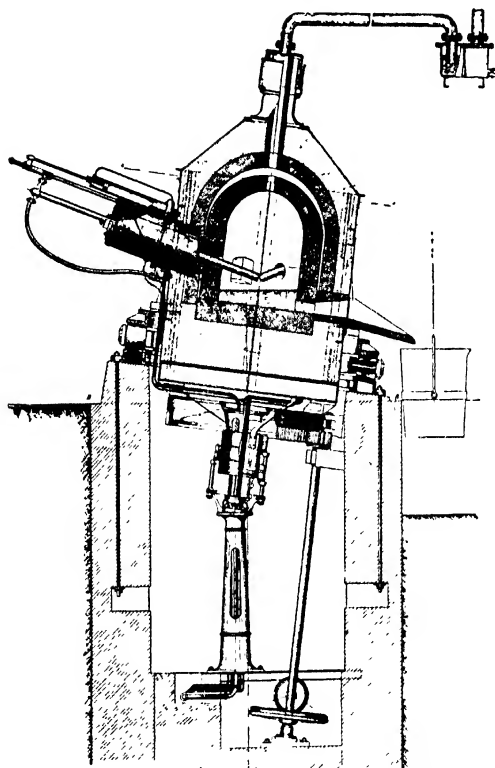
Fig. 179. — Vertical Section of the Stassano Furnace

According to Stassano, the plant at Darfo was shut down for reasons not directly connected with the success of the process.

The Keller furnace[1] for making pig iron is shown in Figure 180. This furnace was seen in operation by the Canadian Commission at Livet, France, in 1904. It consists of two iron castings of square cross-section, forming two shafts communicating with each other at their lower ends by a lateral canal. The castings are lined with refractory material. The base of each shaft is

[1] Haanel's Report, p. 15 (1904).

provided with a carbon block, these two blocks being connected to each other outside the furnace by copper bars. On starting, before there is metal in the canal, the current flows from one block to the other through the copper bar, but when enough metal has been reduced to partially fill the canal, most of the current flows through the melted metal. The electrodes are 1.4 meters long and 85 by 85 centimeters in cross-section. The cost of electrodes per metric ton of pig iron is estimated by Keller at 3.85 francs. The energy absorbed per metric ton of pig iron in a furnace supplied with 11,000 amperes at 60 volts was 0.390 kilowatt-year for the run, and with a smaller furnace supplied with 7000 amperes at 55 volts it was 0.186 kilowatt-year for the run.[1]

Fig. 180. — Section of the Keller Furnace for Reducing Iron Ore

Following the tour of inspection by the Canadian Commission, an investigation was carried out for the Canadian government in 1906 by Héroult, to see (1) whether magnetite could be economically smelted by the electrothermic process; (2) whether ores containing sulfur, but not manganese, could be made into pig iron of marketable composition; and (3) whether charcoal could be substituted for coke. The furnaces were slightly modified as the investigation proceeded, and the final form is shown in Figure 181. It consists of a cylindrical iron casting $\frac{1}{4}$ inch thick, bolted to a bottom plate of cast iron 48 inches in diameter. The casting was made in two sections bolted together by angle irons. In order to make inductance small, the magnetic circuit was broken by replacing a vertical strip of 10 inches width in the casting by copper. Rods of iron were cast into the bottom plate to secure good contact with the carbon paste rammed into the lower part of the furnace. The electrodes, 6 feet long and 16 by 16 inches in cross-section, were manufactured by a process of Héroult's and

[1] Haanel's Report, p. 20 (1904).

were imported from Sweden. The pipe k was for the purpose of cooling the electrode holder by a current of air. The current was between 4000 and 5000 amperes at 36 to 39 volts, and the power factor was 0.919. The consumption of the electrode in these experiments was 8.9 kilograms per metric ton of pig iron produced. The yield per unit of energy varied somewhat, but was approximately 0.25 kilowatt-year of 365 days per metric ton of pig iron (10 kg./kw.-day).

FIG. 181 — SECTIONS OF THE HÉROULT EXPERIMENTAL FURNACE FOR REDUCING IRON ORE

The results of these experiments were :

1. Canadian ores, chiefly magnetites, can be as economically smelted as hematites by the electrothermic process.

2. Ores of high sulfur content can be made into pig iron containing only a few thousandths of one percent of sulfur.

3. The silicon content can be varied as required for the class of pig iron to be produced.

4. Charcoal, which can be cheaply produced from mill refuse, or wood, which could not otherwise be utilized, and peat coke, can be substituted for coke without being briquetted with the ore.

5. A ferro-nickel pig can be produced practically free from sulfur, and of fine quality, from roasted nickeliferous pyrrhotite.

6. Titaniferous iron ores containing up to five percent can be successfully treated by the electrothermic process.

These results demonstrated the feasibility of applying the electrothermic process to the reduction of iron ores.[1] All that was necessary to put it on a commercial basis was the construction of a furnace that could be economically and successfully used in practice. This was undertaken by three Swedish engineers, Messrs. Grönwall, Lindblad, and Stålhane, at Domnarfvet, Sweden. Seven furnaces were constructed and tested before

[1] Haanel, Report on Exps. at Sault Ste Marie, Ont., p 97 (1907).

arriving at the one which they considered practical and commercial. This required over two years and an expenditure of $102,000. A vertical section of the furnace is shown in Figure 182, from which the general construction is perfectly obvious. It evidently resembles somewhat Stassano's original furnace, and, like his, is started as an ordinary blast furnace.[1] The crucible is 2.25 meters in diameter and 1.5 meters high. The most important point in the construction is the manner in which the electrodes are brought into the melting chamber. As seen from the section, they enter through that portion of the roof of the crucible that does not come in contact with the charge, and pass into the charge at the slope formed by the materials of which it is composed. The electrodes dip into the charge, but not into the melted iron beneath it.[2] Experiments had shown that the brickwork lining around the electrodes was always destroyed if brought in contact with the charge, even when the electrodes were water cooled. The brickwork composing the lining of the roof of the melting chamber was cooled by forcing against it, through tuyères, the comparatively cool tunnel-head gases. The heat absorbed by these gases is given back to the charge above.

A three-phase current is supplied to three electrodes 11 by 22 inches in cross-section and 63 inches in length. The water-cooled stuffing boxes through which the electrodes enter the

Legend

▨ Ordinary Brick   ▨ Fire Brick   ▨ Magnesite

FIG. 182. — SECTION OF FURNACE AT DOMNARF-VET, SWEDEN, FOR REDUCING IRON ORE

[1] For the evolution of the furnace, and dimensions, see Met. Chem. Eng. **8**, 11 (1910).
[2] Assar Grönwall, Electroch. Met. Ind. **7**, 420 (1909).

melting chamber are provided with devices to prevent the hot gases under pressure from leaking out around the electrodes. The yield of pig iron is 10 kg./kw.-day, the consumption of charcoal is 37 percent of the weight of pig iron produced, and the electrode consumption, 0.8 percent.[1]

This type of furnace has proved a permanent success, and many have since been built. There are nineteen in Sweden, and eleven distributed through Norway, Switzerland, Italy, and Japan.

The Domnarfvet furnace was designed for the use of charcoal, but tests have shown that mixtures of coke and charcoal up to 50 percent coke can be used, while higher percentages of coke give poor results. Coke alone would require a different and as yet unknown design. The following are the present requirements per metric ton of pig iron, and the composition of the gas:[1]

Iron ore	1720 kg.	CO_2	25 percent
Limestone	60 kg.	CO	65 percent
Charcoal	370 kg.	H_2	8.5 percent
Electrodes	8 kg.	N_2	1.5 percent
Power	2400 kw.-hr.		

From 1909 to 1914 experiments on reducing iron ore in a 1500-kilowatt shaft furnace were carried out at Héroult, California, but the process was given up.[2] Electric pig iron with low phosphorus and sulfur has been made in this country from steel scrap, and the same process had great development in France during the war. This consisted in melting the steel and adding the necessary carbon.[3] The product is called synthetic cast iron.

Furnaces without shafts, such as ferroalloy furnaces, are also used in reducing iron ore, and according to Turnbull produce iron more cheaply than shaft furnaces, which, unless the gases are used, are " complicated, expensive, and unnecessary . . ." The cost of pig iron smelted in 7000- to 10,000-kw., rectangular open-top furnaces has been estimated at about \$40 per net ton.[4] Smelting can also be done in induction furnaces under certain conditions and compete with the blast furnace.[5] One advantage of

[1] De Geer, Chem. Met. Eng. **24**, 433 (1921).

[2] Keeney, El. J. **17**, 206 (1920) ; Bureau of Mines Bull. 67 (1916).

[3] Turnbull, Tr. Am. Electroch. Soc. **32**, 119 (1917). Keller, *ibid.*, **37**, 189 (1920).

[4] Gosrow, Tr. Am. Electroch. Soc. **41**, 120 (1922). For relative advantages of open- and closed-top furnaces, see the discussion following this paper.

[5] Rodenhauser, Schoenawa, and Vom Baur, *Electric Furnaces in the Iron and Steel Industry*, p. 349 (1920).

the induction furnace is that the raw material may be finely divided.

ELECTROTHERMIC STEEL REFINING

The refining of steel is not confined to the use of water power, and on this account, and because of the high quality of the product, the number of steel-refining furnaces has increased rapidly during recent years. There are now approximately 1000 in operation in the world. The advantages of electric furnaces are the following : [1] the rapidity of heating, the accurate control of temperature, freedom from contamination by gases of combustion, the high degree of refining possible from cheap raw material, and the smaller quantity of ferroalloys required.

The process of refining [2] consists in holding the liquid steel in contact with a slag which is able to reduce the impurities to the desired amounts. The principal impurities are carbon, sulfur, and phosphorus. First a slag consisting of lime, iron oxide, a little silica, and sometimes some calcium fluoride to make it more fluid, is used. Iron oxide removes carbon as carbon monoxide, and phosphorus is oxidized to the pentoxide and dissolves in the slag. Sulfur is present as iron and manganese sulfides and is soluble in both steel and slag, but the relative amount of sulfur in slag to that in steel increases with the basisity and temperature of the slag. In order to remove sulfur completely it must be converted to a sulfide which is soluble only in slag. Calcium sulfide fulfills this requirement, but it cannot exist in an oxidizing slag, for it would be oxidized to calcium sulfate, and this is acted on by iron to produce iron sulfide, possibly according to the reaction, $CaSO_4 + 4 Fe = FeS + 3 FeO + CaO$. Therefore to remove sulfur, the slag containing phosphorus must be removed and a reducing slag melted in its place. The oxidizing slag must be thoroughly cleaned off, for phosphorus would go back into the steel from a reducing slag. The only difference between a reducing and an oxidizing slag is that the oxidizing slag contains iron oxide and is black, while a reducing slag is white. Slag is made reducing by carbon, ferrosilicon, or calcium carbide. Sulfur can then be removed to as low a value as 0.001 percent. The reactions are approximately as follows:

[1] Rodenhauser, Schoenawa, and vom Baur, *Electric Furnaces in the Iron and Steel Industry*, p. 65 (1920).

[2] Geilenkirchen and Osann, Electroch. Ind. **6**, 405 (1908); Amberg, Electroch. Met. Ind. **7**, 115 (1909) and Tr. Am. Electroch. Soc. **22**, 133 (1912).
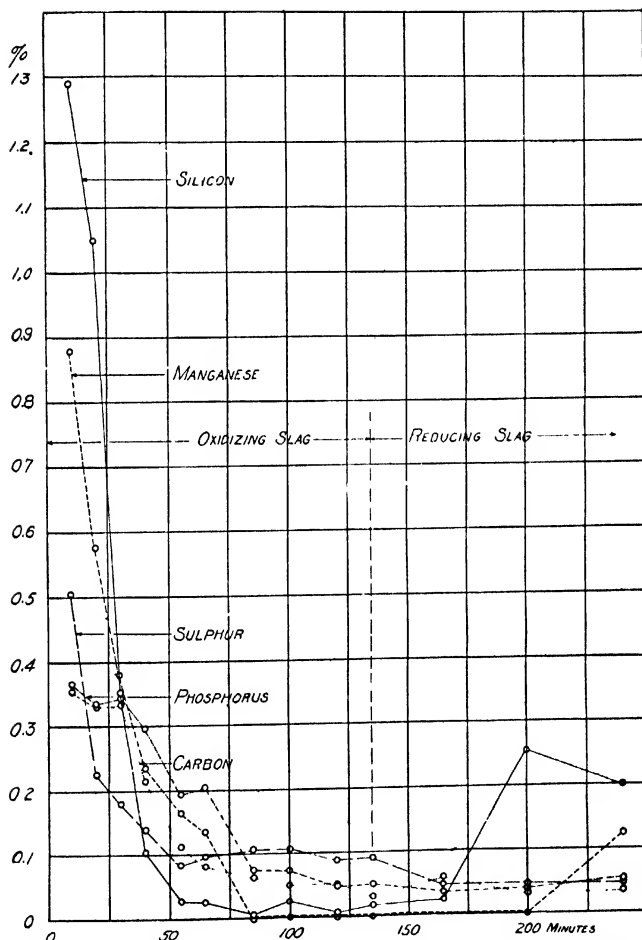
FIG. 183. — GRAPHS SHOWING RESULTS OF A REFINING RUN IN A 200-POUND
HÉROULT FURNACE

$$2\,CaO + 3\,FeS + CaC_2 = 3\,CaS + 3\,Fe + 2\,CO,$$
$$2\,CaO + 2\,FeS + Fe_xSi = 2\,CaS + (x+2)Fe + SiO_2.$$
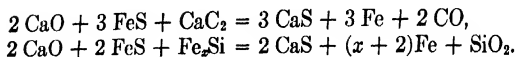
The reducing slag is also necessary to remove oxygen from steel. A sample taken while under an oxidizing slag on solidifying emits gas in small craters, and is found to be full of holes. When deoxidized, it solidifies quietly. Deoxidation up to a certain point is brought about by ferromanganese and ferrosilicon; to make it more complete, a small amount of aluminum is placed in the ladle into which steel is poured from the furnace, and from which the final castings are made. Figure 183 shows the results of a refining run in a 200-pound Héroult furnace.[1]

The linings of steel-refining furnaces in contact with basic slags must of course be basic. Such linings are usually either magnesite brick or magnesite brick with a layer of ground, fused magnesite. The object in using a basic slag is that cheaper ores, containing sulfur and phosphorus, can be used. Acid linings and slags would be used when these two impurities are not present except in small amounts, for they are cheaper in all other respects, such as labor, time, power, overhead, repairs, linings, fluxes, and recarburizers.[2] In all of the arc furnaces to be described the electrodes are water cooled where contact is made with the electric cables and also where they enter the furnace. A cooler called the *Brooke electrode economizer*[3] has been devised for cooling at the furnace roof which cools the gases and prevents the burning of the gases and the electrodes. This is shown in Figure 184. This economizer is said to show a saving of 20 to 50 percent in electrode consumption as compared with the ordinary cooling rings.

The furnace used by Stassano at his works in Turin is the same as the one he finally adopted for re-

A GASES CONTRACTED
B WATER COOLED GAS EXPANSION CHAMBER
C 1ST CONTRACTION OF COOLED GASES
D LARGE COOLING CHAMBER
E CLEARANCE FOR ESCAPE OF COOLED GASES
H COVER

SECTION VIEW OF FURNACE ROOF AND ELECTRODE ECONOMIZER
(Patent applied for)
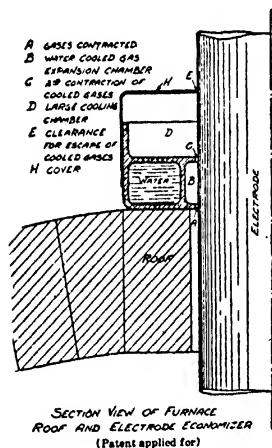
FIG. 184. — BROOKE ELECTRODE ECONOMIZER

[1] Hansen, Electroch. Met. Ind. **7**, 206 (1909).
[2] Stoughton, Met. Chem. Eng. **28**, 986 (1923).
[3] Hodson, Tr. Am. Electroch. Soc. **38**, 321 (1920).

ducing iron ore [1] (Figures 178 and 179). The charge is heated by radiation from arcs formed between three electrodes placed above the charge and supplied with a three-phase current. This furnace also rotates on an axis inclined at 7° to the vertical, in order to mix the charge thoroughly. The lining is magnesite brick.[2] Starting with scrap and oxidized turnings, about one kilowatt-hour is required for one kilogram of finished steel in the 250-horse-power furnaces used at Turin.

A furnace designed by Charles Albert Keller for steel refining, which was put into industrial use in 1907, is shown in Figures 185 and 186. It consists of a crucible with a conducting bottom for one electrode and a vertical carbon rod for the other.[3] Since
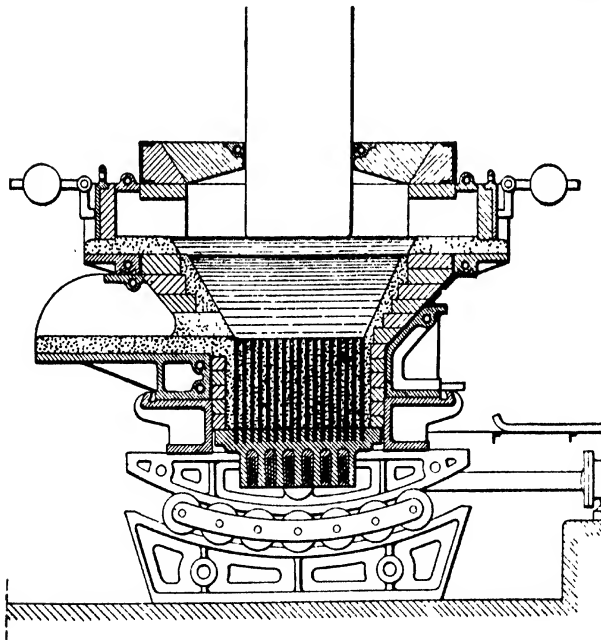
FIG. 185. — VERTICAL SECTION OF THE KELLER STEEL-REFINING FURNACE

[1] Tr. Am. Electroch. Soc **15**, 63 (1909).
[2] Tr. Am. Electroch. Soc. **15**, 86 (1909).
[3] Tr. Am. Electroch. Soc. **15**, 96 (1909).

carbon must not be brought in contact with the melted iron in refining, the bottom must be made conducting without the use of carbon, and this was accomplished by Keller as follows: Iron bars from 1 to $1\frac{1}{4}$ inches in diameter are regularly spaced about 1 inch apart, and are made fast to a metallic plate at the bottom, covering the entire area on which the bath will rest. Agglomerated magnesia is then rammed, while hot, in between the bars. The whole base is surrounded by a metallic casing for water cooling. Electrical contact is made by the lower plate to which the bars are fastened. The furnace is closed by a cover through which the other electrode passes. After several months' use a hearth constructed in this manner was found to be in as good condition as on the first day. The advantage claimed for this arrangement over a furnace with two vertical electrodes is

FIG. 186. — HORIZONTAL SECTION OF THE KELLER STEEL-REFINING FURNACE
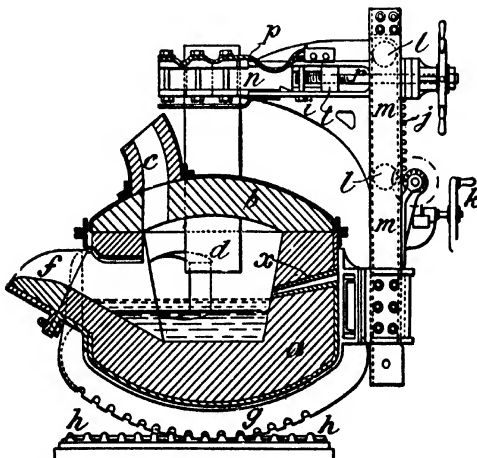
FIG. 187. — VERTICAL SECTION OF THE HÉROULT STEEL-REFINING FURNACE

that the current is more evenly distributed through the charge, and consequently heats it more evenly. Of course, the iron bars are melted at their upper ends where they come in contact with the melted iron to be refined, but the water cooling prevents them from melting for more than a few inches of their length.

The Héroult steel-refining furnace,[1] as shown in Figure 187, consists of a crucible a with a cover b holding a small chimney c. As the figure shows, it is arranged for tilting. d are carbon electrodes, which may be moved in a vertical or in a horizontal direction. In order to use the furnace for Bessemerizing, the tuyères x were originally provided, but were later omitted, as well as the vent c. Arcs are formed between each electrode and the slag, and the circulation of the metal equalizes the temperature. The poorest kinds of scrap, high in sulfur and phosphorus, are refined in this furnace. The following table shows the average refining ability of a $2\frac{1}{2}$-ton furnace at La Praz, Savoy:

TABLE 54

| | PERCENT | | | | |
	Sulfur	Phosphorus	Manganese	Silicon	Carbon
Scrap charged	0.052	0.150	0.638	0.062	0.211
Finished steel	0.006	0.009	0.254	0.172	1.013

For a 5-ton furnace, starting with cold scrap, 600 kilowatt-hours are necessary to partially refine one long ton of steel, and 100 more for the finishing slag. For a 15-ton furnace, less power would be required.

Figure 188 shows a 15-ton three-phase Héroult furnace at the South Chicago Works of the Illinois Steel Company. The steel to be treated is brought directly from the Bessemer converters, and two refining slags are used in the electric furnace, the first an oxidizing slag to take out the phosphorus, and the second, a deoxidizing slag for removing the sulfur and the gases.[2] Power is supplied to the three electrodes by three transformers, each of 750 kilowatts capacity. Two hundred and forty tons of steel are turned out per day in 16 heats. The electrodes, 2 feet in diameter and 10 feet in length, are the largest ever made in one piece. In

[1] Electrochem. Ind. 1, 64 (1902); U S Pat. 707,776 (1902).
[2] Robert Turnbull, Tr. Am. Electroch. Soc. 15, 139 (1909).
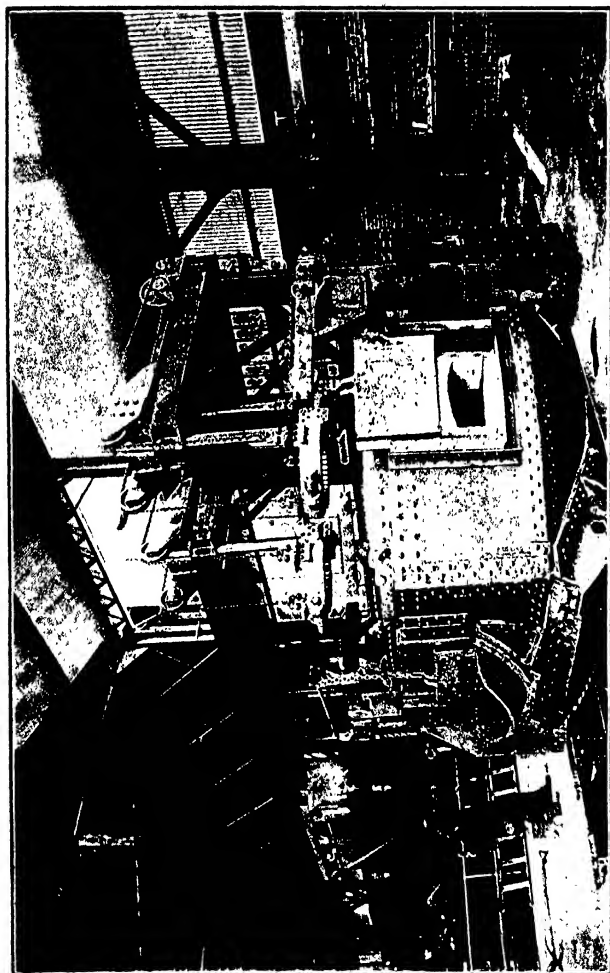
FIG. 188. — THREE-PHASE 15-TON HÉROULT STEEL-REFINING FURNACE AT SOUTH CHICAGO

cold melting and in continuous work, the consumption of electrode is from 60 to 65 pounds per ton of steel, but when the metal is charged in the melted state, the consumption would be reduced to 10 or 15 pounds per ton of steel.   This includes the short ends that cannot be utilized.   The linings last from three months to one year,

depending on the care with which the furnace is run; the roof suffers most, and generally has to be renewed once a month.   The best lining for this furnace is magnesite mixed with basic slag, with tar for a binder.   The roof is a steel-plate frame holding bricks in a flat arch.

In a three-phase Héroult furnace the electrodes are placed equidistant from each other, forming a triangle, while the lining is usually circular in form, consequently the lining is unequally heated and does not wear away at a uniform rate.   This has been improved in the Vom Baur furnace,[1] in which the three electrodes are placed in a straight line and the cross-section of the inner surface of the furnace is so designed that where the slag comes in contact with the walls the temperature is uniform throughout.   The spout is in line with the electrodes. Either three-phase or three-wire two-phase current can be used.

The Ludlum furnace accomplishes the same result[2] in very much the same way.   It increases its efficiency by having a very low roof.

Fig. 189. — Sections of the Girod Steel-refining Furnace

The Paul Girod electric furnace[3] is somewhat similar to the Keller furnace, as seen from Figure 189.   One or more electrodes

[1] Tr. Am. Electroch. Soc. **33**, 237 (1918).

[2] Rodenhauser, Schoenawa, and Vom Baur, *Electric Furnaces in the Iron and Steel Industry*, p. 284 (1920).

[3] Paul Girod, Tr. Am. Electroch. Soc. **15**, 127 (1909).

of like polarity are suspended above the crucible, while the electrode of opposite polarity consists of a number of pieces of soft steel buried in the refractory material of the hearth at its periphery and water cooled at their lower ends. The upper ends come in contact with the bath and are melted to a depth of 2 to 4 inches. About 55 volts are applied to this furnace. For fusing, refining, and finishing a charge of cold scrap in a 2-ton furnace, about 900 kilowatt-hours per metric ton of steel are required, and in an 8- to 10-ton furnace, 700 kilowatt-hours. The electrode consumption is 16 to 18 kilograms per metric ton of steel produced in a 2-ton furnace, and 13 to 15 kilograms in an 8- to 10-ton furnace. The short ends are included as having been used. The lining is magnesite or dolomite brick or paste, and lasts 40 to 50 heats without any repairs whatever. This furnace is also built for three-phase currents.

The Rennerfelt furnace [1] is somewhat similar to the Stassano furnace. The arc is above the bath, but the electrode arrangement, as shown in Figure 190, directs the arc downward to the bath. Two-phase current is used, which can be obtained from three-phase systems by the Scott connection, which consists of two transformers, in which on the three-phase side one transformer has a tap at the middle point and the other a tap giving 87 percent of the full transformer voltage, while the two-phase side may be connected in the normal two-phase manner either independently or interlinked.

FIG. 190. — SECTION OF THE ELECTRODES IN THE RENNERFELT FURNACE

The horizontal electrodes are 3 inches above the bath, and their distance from tip to tip is 18 to 22 inches. The arc is very steady and automatic regulation is unnecessary. In later designs the side electrodes are arranged for tilting in a vertical plane. The furnace is circular when there is one set of electrodes, oval where there are two. A 3-ton furnace with two 375-kilovolt-ampere transformers at 100 volts has 3750 amperes through each side electrode and 5287 amperes through the top electrode. The

[1] Tr. Am. Electroch. Soc. **29**, 497 (1916); **31**, 87 (1917).
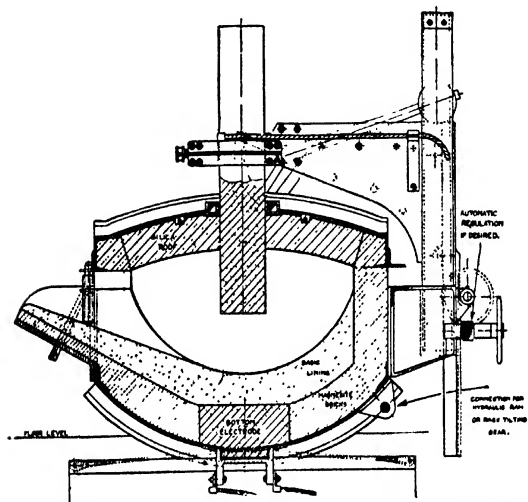
Fig. 191. — Section of the Grönwall Two-phase Steel-refining
Furnace
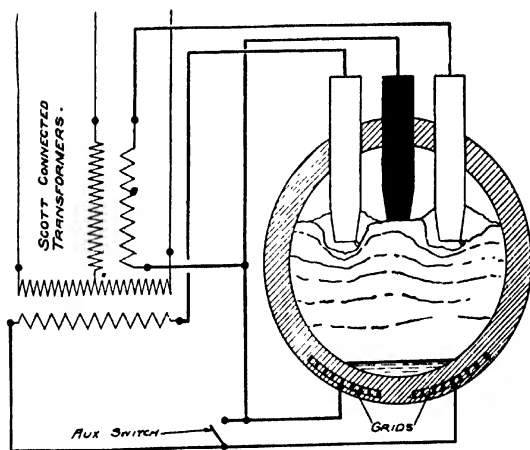
Fig. 192. — Section of the Booth-Hall Steel-refining Furnace

power factor is 0.9. The side electrodes are 5⅛ inches in diameter, the top electrode is 6 inches, both of Acheson graphite.

Melting and refining steel scrap on basic bottoms takes about 700 kilowatt-hours per metric ton and 3 kilograms of electrode.

The Grönwall two-phase arc furnace,[1] shown in Figure 191, has two vertical electrodes passing through the roof, each connected to one phase. The neutral electrode is a carbon block fixed in the bottom of the furnace and is covered by the basic lining. The arcs are consequently independent of each other.

The Greaves-Etchells furnace [2] has the electrodes arranged similarly to those of the Grönwall furnace but is supplied by three-phase current. The high-tension electric supply is transformed by means of a delta-star connection. The leg connected to the hearth maintains 27 volts, each of the other two legs, 60 volts.

The Booth-Hall furnace,[3] shown in Figure 192, also has a conducting bottom. When heating up, the auxiliary electrode, shown in black, is used until the bottom becomes hot enough to conduct, when the auxiliary electrode is disconnected and the grids in the bottom are connected in its place. This furnace is built for single-phase, two-phase, or three-phase circuits. The positions of the electrodes for the three cases are shown in Figure 193. For making steel from the ordinary grade of steel castings, this furnace averages from 500 to 550 kw.-hr. per 2000 lb. of poured steel.

For purely melting operations where slags do not have to be handled, rotating furnaces have been found advantageous, as the heat that is ordinarily lost through the roof is partly saved.

SINGLE PHASE   TWO PHASE   THREE PHASE
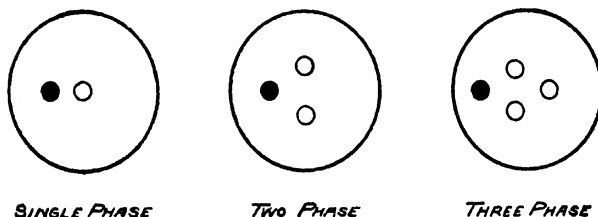
FIG. 193. — DIAGRAMMATIC REPRESENTATION OF ELECTRODE ARRANGEMENT IN BOOTH-HALL STEEL-REFINING FURNACES

[1] Robertson, Met. Chem. Eng. **9**, 573 (1911).
[2] Moore, Chem. Met. Eng. **23**, 825 (1920).
[3] W. K. Booth, Tr. Am. Electroch. Soc. **33**, 247 (1918).

The Booth rotating furnace [1] is a horizontal cylinder with the electrodes in line with the axis. A rocking furnace [2] has been designed and tested by Gillett and Rhoads of the Bureau of Mines and is built by The Detroit Electric Furnace Company. In both of these an arc plays between electrodes above the metal to be melted.

The Baily furnace [3] is of the resistance type. It is built in two forms: (1) a round tilting form, consisting in a vertical cylinder with a heating element of granular carbon placed in an annular trough of silicon carbide. The electrodes enter the trough diametrically opposite each other. (2) A rectangular furnace for melting large tonnage and for smelting. This has two straight resistor troughs. The heating element is above the charge and the heat is reflected down from the roof.

An entirely different class of steel-refining furnaces are those having the melted metal in the form of a ring, forming the secondary of a transformer which is heated by an induced current from a primary coil of copper wire. [4] This type of furnace was patented in 1887 by Colby in the United States and by Ferranti in England. The same principle was applied on a small scale in 1900 by F. A. Kjellin at Gysinge, Sweden, without knowing at the time that it had been patented by others. [5] Kjellin, how-
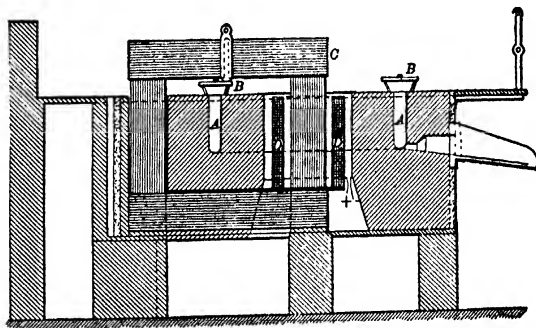
FIG. 194. — VERTICAL SECTION OF THE KJELLIN INDUCTION FURNACE

[1] Booth, Chem. Met. Eng. **21**, 656 (1919).
[2] Met. Chem. Eng. **18**, 583 (1918); Met. Ind. **17**, 320 (1919).
[3] Met. Ind. **17**, 316 (1919); Tr. Am. Electroch. Soc. **32**, 155 (1917).
[4] For a general discussion of induction heating, see page 380.
[5] Kjellin, Tr. Am. Electroch. Soc. **15**, 173 (1909).

ever, seems to have been the first to carry this idea out on a commercial scale. In 1902 a 225-horse-power induction furnace was in operation at Gysinge, with an output of 4 metric tons in 24 hours. This furnace had a magnesite lining in place of silica used in the smaller furnace. A silica lining lasted only about one week, while the magnesite lasted twelve.

Figures 194 and 195 show sections of the Kjellin furnace. The magnetic circuit C is built up of laminated sheet iron. D is the primary circuit, consisting of a number of turns of insulated copper
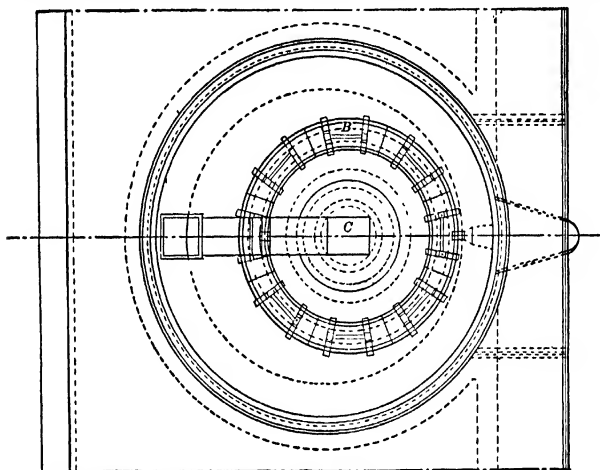
FIG. 195. — HORIZONTAL SECTION OF THE KJELLIN INDUCTION FURNACE

wire or tubing. The ring-shaped crucible A, for holding the melted metal, is made of refractory material. This furnace cannot be started by placing cold scrap in the crucible because of the low induced electromotive force, but an iron ring must be placed in the crucible and melted down, or the crucible must be filled with melted metal taken from another source. The power consumption of the furnace at Gysinge, starting with cold pig iron and scrap, is about 800 kilowatt-hours per metric ton of product. This furnace has been found very satisfactory for making the highest-class steel from pure raw materials.

It is also used for melting ferromanganese before adding to steel, as it is found that less is required if previously melted.

In melting metal in induction furnaces, enough metal must always be left after pouring to complete the circuit. Cold metal can then be added to the metal left behind and melted. One great advantage of induction furnaces over arc furnaces is that in melting there are no appreciable power fluctuations.

The power factor decreases as the charge is increased as previously explained; consequently, the larger the furnace the lower the power factor, for a given frequency. Large furnaces are therefore run on a current of 5 cycles a second. On account
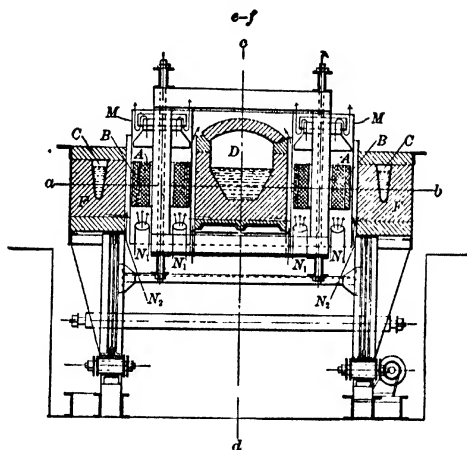
Fig. 196. — Vertical Section of the Röchling-Rodenhauser Induction Furnace

of the absence of electrodes, and the fact that a transformer is an efficient machine, the electrical efficiency of induction furnaces is better than that of any other.

The 3300-pound furnace at Gysinge is operated with 3000 volts on the primary of 295 turns, thus giving 10 volts in the secondary. The transformer is built with a grounded protecting shell to avoid danger from this high voltage. The power input of the furnace is controlled by regulating the field of the generator. The total efficiency in melting iron is from 50 to 80 percent.[1]

The Frick induction furnace resembles the Kjellin furnace,

[1] Engelhardt, Stahl und Eisen, Feb. 1905, p. 205.

but the primary windings are both in the disk and the tube form for the purpose of improving the power factor.[1]

The Kjellin furnace is not adapted to working with dephosphorizing and desulfurizing slags, as the annular ring is not a convenient shape and offers too small a surface to the attack of the slag.[2] A combined induction and resistance furnace was therefore invented by Rodenhauser, known as the Röchling-Rodenhauser furnace.[3] A plan and an elevation of this furnace are
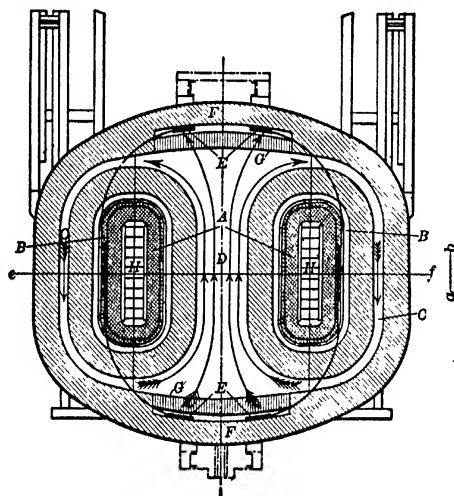
Fig. 197. — Horizontal Section of the Röchling-Rodenhauser Induction Furnace

shown in Figures 196 and 197. *HH* are the two legs of the iron transformer core, surrounded by the primary windings *AA*. Surrounding the legs of the transformer are the two closed circuits of melted metal, forming together a figure 8, in which currents are induced. *BB* are two extra primary coils, from which the current is conducted to the metallic plates *EE*. These are covered by an electrically conducting refractory material, through which the current passes into the main hearth, *D*. The result is that the

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[1] Frick, J. Iron and Steel Inst., 1913, II, p. 297.
[2] Kjellin, Tr. Am. Electroch. Soc. **15**, 175 (1909).
[3] U. S. Pat. 877,739 (1908).

main hearth can be made with a much larger cross-section than the ring in the original Kjellin furnace, and a good power factor can be obtained in large furnaces without such a low periodicity as was necessary with the original induction furnaces. The magnitude of the current from the secondary coils is limited by the carrying capacity of the refractory material G, which would be destroyed if too heavily loaded. These pole plates have been given up in some places because they were more of a nuisance than a benefit.[1] In refining, the furnace is worked as follows: Fluid steel from the converters is poured into the furnace, and burnt limestone and mill scale are added for forming a basic dephosphorizing slag. This is removed, after the reactions are ended, by tilting the furnace. For making rails the phosphorus is reduced sufficiently in one operation, but for the highest-class steel it has to be repeated.

Slag is prevented from entering the narrow channels by placing magnesite brick across the ends of these channels, projecting into the steel a short distance. After removing phosphorus, carbon is added in the pure state when carbon steel is to be made, and a reducing basic slag is formed to remove the sulfur.

Röchling-Rodenhauser furnaces were formerly built for three-phase currents, but these were not successful and two-phase furnaces are built in their place.[1]

BRASS MELTING, FERROALLOYS, AND NON-FERROUS METALS

Brass Melting. — None of the open-channel induction furnaces can be used to melt metals of high conductivity, such as copper, brass, or aluminum, because the large current required would produce the pinch effect and the constant breaking of the circuit would allow the metal to freeze. To melt these metals the furnace has to be designed so that metal is under a high hydrostatic pressure at the place where the pinch effect tends to occur. The pinch effect is then of benefit in producing the necessary circulation. The Hering[2] furnace was the first furnace built on this principle.

Referring to Figure 198, it is seen that the current passes through two channels connected with the metal bath above. The pinch effect causes the metal to rise in the center of these columns, and to descend on the outside. In melting manganese bronze the power consumption is about 400 kw.-hr./ton. The great disadvantage of this furnace is the large amount of cooling water

[1] Styri, Tr. Am. Electroch. **32**, 135 (1917)
[2] Met. Chem. Eng. **9**, 277 (1911); Hering, Tr. Am. Electroch. Soc. **19**, 255 (1911); Gillett, The Foundry, **48**, 486 (1920).
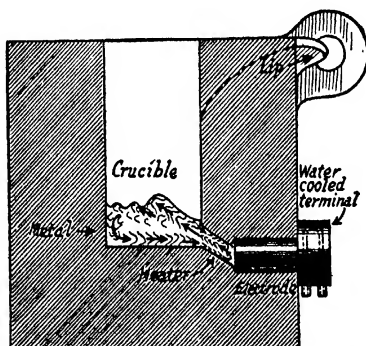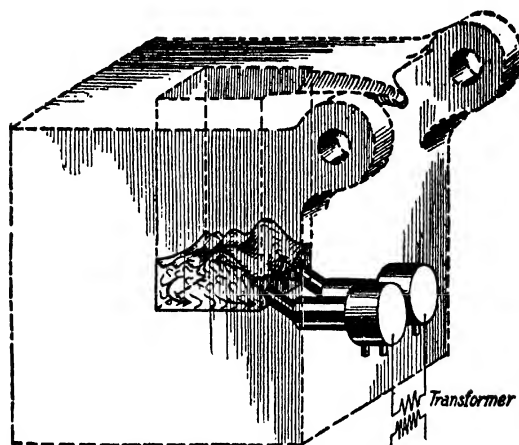
FIG. 198. — THE HERING INDUCTION FURNACE

required to keep the copper electrodes solid, causing large loss in heat.   There is also a large loss in the transformer.

In the Ajax-Wyatt furnace [1] shown in Figure 199, there are no electrodes.   It consists of a cylindrical chamber, in the bottom of which open the two legs of the V-shaped resistor, or secondary,

[1] Northrup, J. Franklin Inst. **190**, 817 (1920); Hering, Tr. Am. Electroch. Soc. **39**, 313 (1921); Gillett, The Foundry, **48**, 486 (1920).

loop. The transformer core is the three-legged type, with the primary wound on the central leg. The transformer is inclosed in a casing and cooled by a blast of air from a small blower.

The standard-size furnace takes 60 kilowatts, and pours 60 pounds of metal per heat. The voltage is 220 single-phase, and at 60 cycles the power factor is 0.81; for a 30-kw. furnace, it is 0.87.

The resistant loop is originally formed by ramming in the lining of high-temperature asbestos cement about a brass casting, which is left in. After slow and careful air drying, the hearth is heated by a gas torch, melted zinc is poured in, and power at a low voltage is applied. When the brass casting has alloyed with the zinc and melted, brass scrap and copper are added to bring the contents to proper composition. When the furnace is shut down, all metal must be drained from the resistor, since if allowed to freeze in it, the lining would be cracked. In starting after a shutdown, the

Fig. 199. — The Ajax-Wyatt Induction Furnace

furnace is heated by a gas flame and melted zinc poured into the resistor. In the 600-pound size the lining will last the pouring of 400 to 600 tons of brass. In the 600-pound furnace the power consumption is about 175 kw.-hr. per ton of yellow brass under best conditions, corresponding to 200–220 kw.-hr. on average operation.

One of the disadvantages of this furnace is its lack in versatility, for a metal of higher conductivity, such as copper, would require a different cross-section in the resistor, and the power factor would not be so good. Also the lining does not stand up well with alloys high in lead.

In 1920 the cost of a 60-kw. furnace was $6500.

Northrup's high-frequency furnace, the principle of which is described above, is made in several different forms. They have between 20 and 40 percent electrothermal efficiency, depending on the size. A 60-kw. furnace with a 600-pound charge of any non-ferrous metal melting below 1200° C. is the largest high-frequency furnace so far constructed.[1]

The Weed induction furnace, shown in Figure 200,[2] is a recent furnace for melting non-ferrous metals. The figure shows the

[1] Tr. Am. Electroch. Soc. **39**, 331 (1921).
[2] Tr. Am. Electroch. Soc. **47**, 233 (1922).
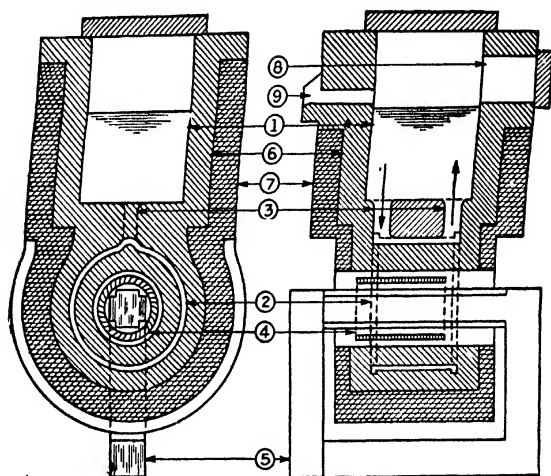
Fig. 200. — Sections of the Weed Induction Furnace

construction. The current flows around the secondary ring (2) without entering the melting chamber. The flow of metal is uni-directional, and is caused by the repulsion between the primary and secondary.

Ferroalloys.[1] — By ferroalloy is meant any alloy of iron rich enough in one or more other elements to be used for introducing these elements into the manufacture of iron and steel. These alloys are in general made from steel turnings mixed with ore containing the other metal and carbon for reducing the ore. This mixture is heated in an arc furnace similar to those now used for the manufacture of calcium carbide, consisting of a boiler-plate shell lined with carbon or magnesite. The walls are usually so far from the electrodes that the reaction zone does not extend to their surface. In this case furnaces usually last two years before requiring repairs.

Some ferroalloys are produced in the blast furnace, but their number is limited because the temperature is too low for reducing some oxides or for melting alloys of high melting point. Also it is difficult to produce alloys containing a high percentage of the special metal, and it is impossible to produce a metal low in carbon.

[1] Anderson, Tr. Am. Electroch. Soc. **37**, 265 (1920).

Consequently up to 1899, when electric furnaces were first used for ferroalloys, their manufacture was confined chiefly to 70 to 80 percent ferromanganese, 10 to 12 percent ferrosilicon, and 30 to 40 percent ferrochromium.[1]

Ferroalloys can have the carbon removed by treating with an oxidizing slag, as in removing carbon from steel.

Ferromanganese is now made in electric furnaces, though at first the high temperature caused such large volatilization losses that this method was for a while given up. The furnace shells are made of about $\frac{1}{2}$-inch boiler plate, mounted on steel rails placed on concrete foundations for allowing air cooling on the bottom as well as on the sides.[2] The shell is lined with firebrick faced with silica brick to a thickness of 18 to 24 inches and inside this is a lining of tar and coke extending over the bottom and sides to a little above the slag line. These linings last from $1\frac{1}{2}$ to 2 years. Furnaces are sometimes cooled by spraying the shells with water. An iron or concrete platform is built on the level of the upper edge of the furnace from which the furnace is charged. The inside dimensions of a three-phase, 25-cycle, 1500 kilovolt-ampere furnace are : 5 feet wide, 5 feet deep, and 12 feet long.[3] There is usually one tap-hole, but occasionally three or four.

The ferromanganese furnaces of the Anaconda Copper Company at Great Falls, Montana, consist of shallow brick shafts 28 by 14 by 9 feet in outside dimensions. The outer walls are red brick lined with firebrick. Inside this is a lining of dead burnt magnesite with pitch as binder 3 feet thick at the bottom, while the thickness of this lining at the walls gradually diminishes to nothing 18 inches above the tap-hole level. Cooling pipes are provided at the bottom with air circulation. The inside dimensions are 22 feet by 9 feet by 6 feet. These furnaces are operated on 60-cycle three-phase current. Two 24-inch (60 cm.) round, amorphous carbon electrodes are used in a common holder on each phase. The average input is 3600 kilowatts.[4]

The charge of ore, limestone, carbon, and steel turnings consists of pieces that can pass through a 2-inch ring. There is an excess of 10 percent carbon for reducing silica and for loss. Coke or anthracite is generally used. The best operating temperature is said to be 1500° C. The loss of manganese by volatilization is

[1] Bureau of Mines Bull. 77, p. 103 (1916).
[2] Darrah, Iron Age, **105**, 1019 (1920).
[3] See also Gosrow, Chem. Met. Eng. **21**, 235 (1919).
[4] Bardwell, Tr. Am. Electroch. Soc. **38**, 333 (1920).

under 4 percent, and the slag contains 15 to 20 percent manganese. This is stored and from time to time is reduced with carbon in a special furnace giving an alloy containing 25 percent manganese and 50 percent silicon.

The yield of 80 percent ferromanganese is about 5 to 8 kg./kw.-day.[1]

Ferrosilicon is made both by the reduction of silica and iron ore with carbon, and with silica, carbon, and steel turnings well mixed. The silica consists of large lumps of ganister or quartzite. The reduction temperature of silica by carbon is 1460° C. but this is lowered to 1200° by the presence of metallic iron.[2] Ferrosilicon is made in various grades containing from 13 percent silicon up to silicon 95 percent pure. The yield for 50 percent ferrosilicon, using steel turnings, is 4 to 5 kg. per kw.-day. This is the grade usually made because lower grades sell at a discount and higher grades evolve objectionable gases.[3] Ferrosilicon containing between 30 and 65 percent silicon has a tendency to disintegrate. The consumption of amorphous-carbon electrodes is about 4 percent of the weight of the product.

Since pure raw materials are used in the manufacture of ferrosilicon, little slag is formed; it consists of silicates of aluminum and calcium or magnesium. As the percentage of silicon in the alloy increases, its specific gravity decreases and it is difficult to obtain separation of metal and slag if the slag is sticky. These slags boil up around the electrodes and are removed there, as they are too viscous for tapping.[4]

A 25 percent ferrosilicon containing between 5 and 10 percent of aluminum can be made from garnet, an aluminum iron silicate, by reduction with carbon.[5] All of the iron is reduced, but only about half of the silica.

Ferrochromium is made by reducing chromite.[6] The reaction is

$$\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 4\text{ C} = \text{Fe} \cdot 2\text{ Cr} + 4\text{ CO}.$$
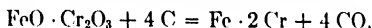
When pure materials are used, no lime is added. Anthracite is the best form of carbon for this reaction as it can be more finely

[1] Gibson, Tr. Am. Electroch. Soc. **37**, 260 (1920); Gosrow, Chem. Met. Eng. **21**, 479 (1919), gives 8.4 kg./kw.-day.

[2] Greenwood, Electroch. Met. Ind. **7**, 119 (1909).

[3] Darrah, Iron Age, **105**, 1170 (1920). See also Bureau of Mines Bull. **77**, p. 173 (1916).

[4] Raven, Tr. Am. Electroch. Soc. **37**, 329 (1920).

[5] Davenport and Thompson, Met. Chem. Eng. **22**, 596 (1920).

[6] Bureau of Mines Bull. **77**, p. 131 (1916).

pulverized and therefore more intimately mixed with the ore. The slag and alloy are tapped from the same hole. The standard grade of alloy contains 6 to 8 percent carbon and 60 to 70 percent chromium. The carbon content can be reduced to 0.5 percent by heating in an arc furnace with a slag of chromite, lime, and fluor spar. The time required depends on the amount of carbon to be removed. The iron content of the alloy increases during the refining, showing that iron oxide is reduced in refining, but not chromium oxide.

The process for producing ferrovanadium differs from that used in the majority of ferroalloys in that 90 percent silicon is used as the reducing agent. This is for the purpose of keeping the carbon content low.

The Electrothermic Metallurgy of Zinc.[1] — In the ordinary retort method of zinc smelting, the ores are calcined to remove carbon dioxide or sulfur. Sulfur must be reduced to less than one percent, which requires a high temperature and a long time. The roasted ore is mixed with 50 percent of fine coke or anthracite and is charged into horizontal fire-clay retorts, which in this country are 8 inches in internal diameter and 8 feet long, holding 50 to 60 pounds of ore. These are heated externally by coal or gas to 1200° C. or more. At this temperature the zinc is reduced and volatilized, and is condensed in a conical fire-clay condenser at one end of the retort. Twenty-four hours are required for a distillation, and the most modern regenerative furnaces have a thermal efficiency of only about 12 percent. Other disadvantages are that the retorts last only 30 to 60 days, and the zinc loss is 10 percent or more.

For these reasons many attempts have been made to smelt zinc in electric furnaces, which can be made in large units and in which high temperatures can easily be obtained.

The reason for the slow progress in electrothermic zinc smelting is the difficulty of condensing zinc vapor to liquid zinc, when the zinc vapor is diluted with gas. In place of liquid zinc " blue powder " is formed to a large extent, which has to be redistilled. There is no trouble in condensing pure zinc vapor. When, however, zinc vapor is diluted with an equal amount of carbon monoxide, it will not begin to condense until the vapor pressure of melted zinc is less than half an atmosphere, which means that the melted zinc must be at a lower temperature than would be necessary for pure zinc vapor, and the more zinc is removed the lower

[1] This discussion is taken largely from Bureau of Mines Bull. No. 208, *The Electrothermic Metallurgy of Zinc*, by M. O'Harra (1923).

the temperature must be. Thus the range of temperature for condensation to the liquid is much narrower than for pure zinc vapor, and requires more careful control. If the vapor is cooled too quickly, it condenses to a solid form corresponding to snow. This is *physical* blue powder. *Chemical* blue powder is produced by a film of sulfide, oxide, or some impurity on the condensed zinc droplets which prevents them from coalescing into one mass. These films may be produced by the oxidizing effect of carbon dioxide or by volatilized iron or silicon. By preheating the charge it is possible to reduce the amounts of water vapor and carbon dioxide given off the charge when heated in the electric furnace, and thus reduce the formation of blue powder. Taking these precautions several investigators have succeeded in getting good yields of liquid zinc in large-scale runs extending over several weeks. The Scandinavian metallurgists, however, have given up trying to produce zinc in one operation, but run the furnaces at a temperature that volatilizes all zinc, and lead, which is collected as blue powder. This is then remelted with a rubbing action to produce liquid metal. The first attempt to reduce zinc electrothermally was that of E. H. and A. H. Cowles in 1885. Their furnace was a horizontal cylindrical retort of non-conducting material well heat-insulated. A carbon plate at one end formed the positive electrode, and the outer end was closed by a carbon crucible which acted as the negative electrode and as a condenser for the zinc. The roasted ore mixed with carbon was sufficiently conducting to carry the current. This furnace was not developed further for zinc smelting but was used for reducing aluminum in the presence of copper.

In 1892 C. G. P. de Laval began work on electric zinc smelting and later took out patents on a furnace for this purpose. The pulverized roasted ore mixed with carbon, or raw sulfide ore mixed with iron, is charged through an opening at one end of a rectangular furnace heated by radiation from an arc formed between two electrodes above the charge. The zinc passes out to a condenser and the residue is tapped. Production with this furnace began in 1903–4 at Trollhättan, Sweden, and Sparsborg, Norway, with raw material consisting of drosses and scrap zinc; results as to condensation and recovering from ore were very poor. Later the radiating arc was replaced by a buried arc of 350 hp. at 100 volts, but a full description of this furnace has not been published. The power required by the new type furnace for smelting ore was 1078 kw.-hr. per ton of ore (10.5 kg./kw.-day), including the power for resmelting the blue powder but not that for refining

crude zinc.   With the old type the power required was 70 percent more.

In 1913, thirteen 1000-hp. furnaces and eight 500-hp. had been built at Trollhättan.   Successful ore-smelting furnaces with a capacity of 12,000 kg. of ore per 24 hours have been built.

In this country important experiments have been carried out by ·W. McA. Johnson.   His final type is shown in Figure 201.
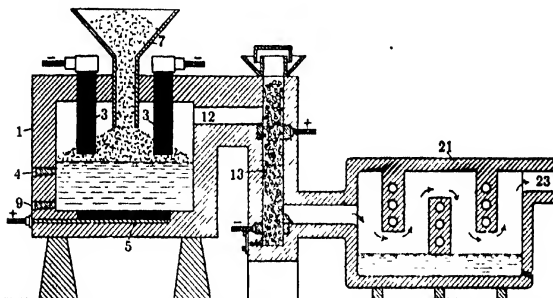
FIG. 201. — THE JOHNSON CONTINUOUS ZINC FURNACE (U. S. PAT. REISSUE 13,208): 1, FURNACE, 3, ELECTRODES; 4, SLAG TAP, 5, ELECTRODE; 7, HOPPER; 9, TAP-HOLE; 12, PASSAGE TO CONDENSER; 13, COKE; 21, CONDENSER

Metal and matte were removed through the tap-hole 9 and slag through 4.   The electrically heated column of coke 13, for the purpose of reducing carbon dioxide to monoxide, was later found unnecessary.

The average energy consumption for a charge of mixed ore and slimes was 1490 kw.-hr. per 2000 lb. (14.6 kg./kw.-day).   The theoretical energy consumption with efficient pre-reduction is per 2000 lb. :

> (Zn 29 percent) calcined zinc ore 264 kw.-hr.
> (Zn 44 percent) calcined zinc ore 565 kw.-hr.
> (Zn 70 percent) calcined zinc ore 900 kw.-hr.

The electrode consumption was 6.05 lb. per 2000 lb. of ore treated.

Extensive experiments were carried out in 1908 at Nelson, British Columbia, for the Canada Zinc Company by F. T. Snyder, in a 10-ton plant in a shaft furnace.   This plant operated for about a year, when it was shut down on account of mechanical troubles with furnace construction, operation, and electrode breakage. Another furnace to take 1500 kw. was designed to overcome these

difficulties and was tested at Chicago. It had a capacity of 35
tons of ore a day; the power consumption was 900 kw.-hr. per ton
of ore (24.1 kg./kw.-day). Though this furnace was said to be
successful, after a short run it was put to other uses.

A process differing radically from those mentioned so far was
proposed in 1914 by C. H. Fulton, and tested at East St. Louis from
1916 to 1918. The ore is mixed with an excess of fine coke and
sufficient hot tar or pitch to act as a binder. A typical mixture
would be 100 parts ore, 60 parts coke, and 18 to 20 parts pitch;
this mixture is then formed into briquettes at a pressure of 500 to
1000 lb./sq. in. which are baked at 450° to 500° C. to drive off
volatile hydrocarbons, leaving porous briquettes. These bri-
quettes were heated in an electric furnace in which they formed the
resistor. They were cylindrical, $9\frac{1}{4}$ inches in diameter and 21 inches
long, and contained 50 pounds of ore. The three-phase furnaces
contained 36 briquettes in 12 columns of three each, placed in two
concentric circles with four connected to each phase in the Y-con-
nection. These briquettes retain their shape during the distilla-
tion; the residue is prevented from forming a slag and is in an
ideal condition for blast-furnace treatment to recover lead, copper,
and precious metals. Experiments with this process were favor-
able and were stopped on account of the war.

Tin, Nickel, and Copper. — Experiments have been made in
England on the electrothermic reduction of tin,[1] but it is probably
not in use at present. The smelting of copper and nickel, however,
seems to be carried out to a limited extent. There are apparently
no difficulties in treating nickel and copper in the electric furnace.

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[1] Bureau of Standards Bull. No. 77, p. 101 (1916).

CHAPTER XX

THE FIXATION OF ATMOSPHERIC NITROGEN

Introduction. — Nitrogen, though chemically an inert element, is of great importance to plant and animal life. It forms 80 percent by volume of the atmosphere, but changing atmospheric nitrogen to a combined state for use in fertilization or in the chemical industries was not begun until 1905. This was a problem of the greatest importance, as the nitrogen removed from the soil by crops must be replaced either by adding it in the form of some nitrogen compound or by raising a crop, such as clover, that assimilates the nitrogen of the air by means of a certain kind of bacteroid existing on the root of the plant. Consequently, Chili saltpeter is used in large quantities for fertilization, but as this supply cannot last indefinitely,[1] the discovery of some other means of supplying the demand became imperative.

At present there are three different methods in operation of combining atmospheric nitrogen. The first method consists in heating calcium carbide in pure dry nitrogen to between 700° and 800° C., whereby nitrogen is absorbed, forming calcium cyanamide, according to the reversible reaction:

$$CaC_2 + N_2 \rightleftharpoons CaCN_2 + C.$$
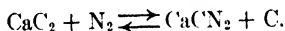
The second method consists in oxidizing nitrogen to nitric oxide in the high-tension arc and absorbing the oxide in water or in an alkaline solution, and the third and most recent method is the direct synthesis of ammonia from its elements. There are also a number of methods that are still in the experimental stage.[2] The two most important of these are the *Serpek process* using the reaction:

$$Al_2O_3 + N_2 + 3 C = 2 AlN + 3 CO,$$
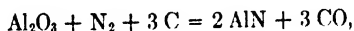
[1] According to Partington and Parker, *The Nitrogen Industry*, p. 74 (1923), the Chili deposits are adequate for meeting all demands for a century or more.

[2] Norton, Special Agents Series No. 52, Bureau of Manufactures, *Utilization of Atmospheric Nitrogen* (1912).

and the *Bucher process* which makes cyanide according to the reaction:

$$Na_2CO_3 + 5C + N_2 = 2NaCN + 3CO.$$
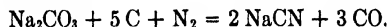
Absorption by Calcium Carbide. — According to Moissan, pure carbide is unaffected by nitrogen at 1200° C.[1] The discovery that nitrogen is absorbed by commercial calcium carbide and barium carbide was patented in 1895 by Adolph Frank and N. Caro.[2] In the case of barium carbide 30 percent forms cyanide in place of cyanamide,[3] while in the case of calcium only a trace of cyanide is formed.

Since 1895 this reaction has been the subject of a number of investigations. With regard to the temperature required, it has been shown that finely powdered carbide must be heated to from 1000° to 1100° C. to bring about complete transformation to cyanide. At 800° to 900° some nitrogen is absorbed, but the reaction ceases before all the carbide is used up.[4] By the addition of other calcium salts, such as calcium chloride, or, to a less extent, calcium fluoride, complete nitrification can be produced at 700° to 800° C.[5] That the commercial carbide can be completely nitrified at 1100° is due to the presence of calcium oxide.[6] Commercial calcium carbide containing 75 to 80 percent carbide can be made to take up 85 to 90 percent of the theoretical amount of nitrogen, forming a black mass of calcium cyanamide, lime, and carbon containing 20 to 23.5 percent of nitrogen. Pure calcium cyanamide contains 35 percent nitrogen. The reaction by which it is made is accompanied by a large evolution of heat, which of course is advantageous in its manufacture. According to Caro, this heat is sufficient to cause the reaction to proceed of itself when once started.[7]

The system consisting of calcium carbide, calcium cyanamide, carbon, and nitrogen would be monovariant if the reaction were that given above, that is, there should be a definite pressure of

[1] C. r. **118**, 501 (1894).

[2] Frank, Z. f. angew. Ch. **19**, 835 (1906). According to Partington and Parker, the German chemist, F. Rothe is the discoverer of this process. — *The Nitrogen Industry*, p. 190 (1923).

[3] Erlwein, Z. f. angew. Ch., p. 533 (1903).

[4] Foerster and Jacoby, Z. f. Elektroch. **15**, 820 (1909).

[5] Polzenius, Chem. Ztg. **31**, 958 (1907); Bredig, Z. f. Elektroch. **13**, 69 (1907).

[6] Foerster and Jacoby, Z. f. Elektroch. **13**, 101 (1907).

[7] N. Caro, Z. f. angew. Ch. **22**, 1178 (1909).

nitrogen in equilibrium with the solid phases at a given temperature. It is found, however, that the nitrogen pressure is dependent on the quantity of nitrogen absorbed as well as on the temperature. This indicates the presence of a solid solution.[1]

Furthermore it is probable that the reaction is not as simple as that given in the equation, but it may take place in two stages represented by the equations:[2]

$$CaC_2 = CaC + C,$$
$$CaC + N_2 = CaCN_2.$$
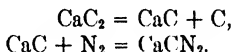
The velocity of absorption of nitrogen is proportional to the pressure, other conditions being constant.[3]

Calcium cyanamide acts in some cases as the calcium salt of cyanamide: $Ca = N - C \equiv N$, and in others as the calcium salt of the diimide:

$$C\underset{N}{\overset{N}{\diagdown}}Ca.$$
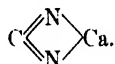
With superheated steam the nitrogen is changed to ammonia according to the reaction

$$CaCN_2 + 3 H_2O = CaCO_3 + 2 NH_3$$
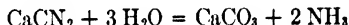
with a yield 99 percent.[4] Dicyandiamide, a compound containing 66 percent nitrogen, can be made by treating calcium cyanamide with water. It has the appearance of ammonium chloride, and is probably formed by the following reaction:

$$2 CaCN_2 + 4 H_2O = 2 Ca(OH)_2 + (CNNH_2)_2.[5]$$
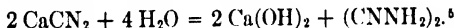
Calcium cyanide can be made from technical calcium cyanamide by melting with a suitable flux, such as sodium chloride, according to the following reversible reaction:

$$CaCN_2 + C \rightleftarrows Ca(CN)_2.$$
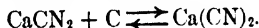
According to Landis[6] the manufacture of cyanide by this

[1] Le Blanc and Eschmann, Z. Elektroch. 17, 20 (1911). See also Thompson and Lombard, Met. Chem. Eng. 8, 617 (1910).
[2] Erlwein, Warth, and Beutner, Z. Elektroch. 17, 177 (1911).
[3] Bredig, Fraenkel, and Wilke, Z. Elektroch. 13, 612 (1907).
[4] Erlwein, Z. f. Elektroch. 12, 551 (1906).
[5] Z. f. angew. Ch., p. 520 (1903).
[6] Tr. Am. Electroch. Soc. 37, 653 (1920). See also Freeman, Can. Chemist and Met. 6, 129 (1922).

reaction was not a success abroad, but the American Cyanamid Company started a plant for this purpose in 1916 which has produced large quantities of cyanide for leaching ores. In carrying out this transformation some nitrogen is lost as free nitrogen and causes foaming in the fused mixture of cyanide and chloride, but the presence of a small amount of calcium carbide is said to stop it entirely. The mixture used at first contained two parts of salt to one of lime-nitrogen, but the salt was gradually diminished until there was less salt than lime-nitrogen in the mixture. Two grades are made, containing respectively 36 and 45 percent equivalent sodium cyanide, with over 90 percent nitrogen efficiency. Calcium cyanide is probably formed.

The fused mixture must be cooled quickly, otherwise the cyanide reverts to the cyanamide. A continuous arc furnace is used, in which the mixture is rapidly fused and drawn off.

The carbide used for making calcium cyanamide is ground in an atmosphere of nitrogen until it will pass a screen of 100 meshes to an inch and is placed in a pasteboard container in a cylindrical iron drum holding from 0.5 to 2.5 tons of carbide. A smaller pasteboard tube is placed along the axis of the cylinder for protecting the small carbon rod which carries the heating current. This rod passes out of the iron top through a tight, insulated joint. The lower end of the rod makes electrical contact at the conducting bottom of the furnace.

At Muscle Shoals the ovens are 4 ft. 4 in. outside diameter by 2 ft. 2 in. inside diameter by 5 ft. 4 in. deep, and consist of a steel shell with a 9-inch lining of firebrick. The cylindrical pasteboard or paper container is 2 ft. 6 in. in diameter, while the smaller tube is 3 in. in diameter. The charge consists of 1600 lb. of pulverized carbide. The carbon electrode is $\frac{5}{8}$ in. in diameter and 6 ft. 6 in. long.

After filling the furnaces with nitrogen, a current of 200 to 250 amp. at 100 volts is applied for 20 minutes, and is then reduced to 50 volts and 100 to 150 amp. for 12 hours. The current is then shut off and the reaction is allowed to continue for 28 hours longer. The temperature attained is about 2000° F. About three times the theoretical amount of nitrogen is used, made by the Claude process of fractionating liquid air.

On nitrifying, the carbide changes to a hard block, which is easily removed on account of the pasteboard containers, which do not char until after the hardening of the charge.

The following is a typical analysis of the lime nitrogen :

	PERCENT		PERCENT
CaCN$_2$	63	SiO$_2$	3
CaC$_2$	2	MgO	2
CaO	13	Fe$_2$O$_3$ and Al$_2$O$_3$	2
CaS	1	Miscellaneous	3
C	11		

The product is allowed to cool, is ground to powder, is treated with water to decompose the carbide, and then with oil to make it dustless.[1]

According to a two weeks' test at the U. S. Nitrate Plant No. 2 at Muscle Shoals,[2] 1 kw.-hr. produced 3.27 kg. of calcium cyanamide, including the production of the carbide required. The cost per 2000 lb. of lime-nitrogen with the plant operating at full capacity was estimated at \$44. This leaves out interest on the investment, depreciation, taxes, and insurance. Of this \$44, \$12.4, or 35.5 percent, is for power at the rate of \$0.0074 per kw.-hr.

In Germany the carbide is placed in sheet-iron containers and run into airtight ovens heated on the outside by gas. Nitrogen is passed through the ovens. In Sweden a continuous process is used, in which a mixture of carbide, quicklime, and calcium fluoride is raked mechanically over shelves in a vertical furnace in which it is heated by a row of electric arcs.[3]

Besides lime and carbon, there are impurities in technical cyanamide, consisting of nitrogen compounds, such as urea, guanidine, and calcium carbamate. In fresh samples these impurities are small in quantity, but increase on standing or by the presence of water vapor. All of these substances are easily assimilated by plants.

The manufacture of calcium cyanamide was begun at Piano d'Orta, Italy, in 1905, and by the American Cyanamid Company at Niagara Falls in Canada in 1909. The capacity of this plant since the outbreak of the war is 64,000 tons of lime-nitrogen per year.

The Oxidation of Nitrogen. — Priestley[4] was the first to observe that electric sparks in air produced an acid, though he mistook it for carbonic acid. Later Cavendish[5] repeated the experiments

[1] Landis, Met. Chem..Eng. **13**, 216 (1915); Fairlee, Chem. Met. Eng. **20**, 8 (1919).

[2] Chem. Met. Eng. **21**, 66 (1919).

[3] Partington and Parker, *The Nitrogen Industry*, p. 196 (1923).

[4] Experiments and Observations on Different Kinds of Air, **4**, 286. Preface dated 1779. Also Ostwald, *Elektrochemie*, p. 11.

[5] Phil. Trans. **75**, 372–384 (1797). Also Alembic Club Reprints, No. 3, p. 39.

and showed the true nature of the acid produced, which is now known to be a mixture of nitrous and nitric acids. From the time of Cavendish until within the last twenty years nothing of importance was done toward explaining this phenomenon. Since 1890, however, it has received considerable attention, so that now, principally due to the work of Nernst and Haber, the conditions under which the reaction $N_2 + O_2 \rightleftharpoons 2\ NO$ takes place are well known.

Nernst and his assistants have measured the thermal equilibrium concentrations of nitrogen, oxygen, and nitric oxide at different temperatures with the results in Table 55.[1]

TABLE 55. PERCENT BY VOLUME OF NITRIC OXIDE IN THE EQUILIBRIUM MIXTURE FORMED FROM AIR

DEGREES ABSOLUTE	PERCENT NO		OBSERVER
	Observed	Computed	
1811	0.37	0.35	Nernst
1877	0.42	0.43	Jellinek
2023	0.52 to 0.80	0.64	Jellinek
2033	0.64	0.67	Nernst
2195	0.97	0.98	Nernst
2580	2.05	2.02	Nernst-Finckh
2675	2.23	2.35	Nernst-Finckh

The values in the third column were computed by the van't Hoff equation, with Berthelot's value of $-21,600$ calories for the heat of the reaction. These experiments show that at the temperatures given the velocity of decomposition is so low that the gas can be cooled without decomposition of the nitric oxide already formed.

The free energy of the reaction is given by the equation [2]

$$\Delta F = Q - RT \log \frac{p_{NO}}{p_{N_2}^{\frac{1}{2}} \cdot p_{O_2}^{\frac{1}{2}}} + 2.45\ T,$$

in which $Q = -21,600$ calories per mol of NO. By means of this equation the percent of nitric oxide corresponding to the equilibrium at any temperature can be computed by placing the right-hand side equal to zero, which is the equilibrium condition. The experiments of Finckh were carried out by exploding air

[1] Z. f. anorg. Ch. 49, 213 (1906).
[2] Haber, *Thermodynamics of Technical Gas Reactions*, p. 105 (1908).

mixed with detonating gas; the others by drawing air through platinum or iridium tubes heated electrically. The good agreement between the calculated and observed values shows that at least in these experiments the nitric oxide formed is due only to the high temperature, as the concentration is that required by thermodynamics.

. This reaction is bimolecular between 650° C. and 1750° C.,[1] that is to say, it should be written $N_2 + O_2 = 2 NO$. Le Blanc and Nüranen, however, have found that above 3000° C. the reaction is monomolecular.[2] Tables 56 and 57 give the velocities of the reaction in both directions at different temperatures.[1]

TABLE 56. TIME IN MINUTES NECESSARY TO DECOMPOSE PURE NITRIC OXIDE AT ATMOSPHERIC PRESSURE, HALF INTO NITROGEN AND OXYGEN

DEGREES ABSOLUTE	TIME IN MINUTES		DEGREES ABSOLUTE	TIME IN MINUTES	
900	7.35	10^3	2100	1.21	10^{-1}
1100	5.80	10^2	2300	8.40	10^{-5}
1300	4.43	10^1	2500	5.76	10^{-6}
1500	3.30		2700	3.92	10^{-7}
1700	2.47	10^{-1}	2900	3.35	10^{-8}
1900	1.74	10^{-2}	3100	2.25	10^{-9}

TABLE 57. TIME REQUIRED TO PRODUCE FROM AIR ONE HALF THE POSSIBLE AMOUNT OF NITRIC OXIDE

DEGREE ABSOLUTE	TIME IN MINUTES		DEGREES ABSOLUTE	TIME IN MINUTES	
1500	1.81	10^2	2500	1.77	10^{-4}
1700	5.90	10^1	2700	8.75	10^{-6}
1900	2.08		2900	5.75	10^{-7}
2100	8.43	10^{-2}	3100	3.10	10^{-8}
2300	3.75	10^{-3}			

From these results it would appear that the best yield of nitric oxide would be obtained by heating the gas to the highest temperature from which it could be chilled so suddenly that decomposition would not take place. It has been shown, however, that nitric oxide can be produced by the silent discharge of electricity where there is very little elevation of temperature.[3] This fact

[1] Jellinek, Z. f. anorg. Ch. **49**, 229 (1906).
[2] Z. f. Elektroch. **13**, 303 (1907).
[3] Warburg and Leithäuser, Ann. d. Phys. (4) **20**, 743 (1906), and **23**, 209 (1907).

suggested to Haber and Koenig [1] the possibility of obtaining better yields by using a comparatively cool arc, which could be realized by inclosing it in a tube surrounded by water. Below 3000° C. any oxide produced by the impact of electrons would not be decomposed rapidly by the heat even if the concentration due to the electrical effect were greater than that due to the thermal. In fact they found that by using a cooled arc and by reducing the pressure to the most favorable value of 100 millimeters, concentrations of nitric oxide were obtained which could be explained thermally only on the assumption that the thermal equilibrium corresponding to over 4000° absolute had been obtained and that the gas had been chilled suddenly enough to preserve it. Such a

TABLE 58. CONCENTRATIONS OF NITRIC OXIDE OBTAINED AT 100 MM. PRESSURE BY AN ARC INCLOSED IN A COOLED TUBE

INITIAL GAS MIXTURE IN PERCENT BY VOLUME		$K = \dfrac{pNO}{p^{\frac{1}{2}}O_2 \cdot p^{\frac{1}{2}}N_2}$	NO CONTENT IN PERCENT BY VOLUME	THERMODYNAMICALLY COMPUTED TEMP ABS.	
O_2	N_2			Haber	Nernst
20.9	79.1	0.284	9.8	4365	4334
48.9	51.1	0.337	14.4	4686	4650
44.4	55.6	0.337	14.3	4686	4650
75.0	25.0	0.357	12.77	4805	· 4767
81.7	18.3	0.397	12.1	5042	5000

high temperature in their arc seemed impossible; consequently the oxide must have been produced directly by the impact of ions. Table 58 gives the concentrations of nitric oxide obtained with the temperature corresponding, on the improbable assumption that this concentration corresponds to a thermal and not to an electrical equilibrium. The temperatures were computed both by Haber's formula given above and by the van't Hoff formula as used by Nernst.

In later experiments as high as 17.8 percent nitric oxide was obtained.[2] It was further found that the same concentration is obtained under similar conditions from either nitric oxide or from air and oxygen, showing that we have in this case an electrical equilibrium. If the temperature is too high, the electrical equilibrium is obliterated by the thermal. On the other hand, the

[1] Z. f. Elektroch. **13**, 725 (1907).
[2] Z. f. Elektroch. **14**, 689 (1908).

electrical energy necessary to produce ionization increases considerably when the temperature falls below white heat. There will therefore be a most favorable region of temperature within which the nitric oxide produced by the impact of ions will not be decomposed and when too much electrical energy is not required for ionization. It would, therefore, seem that the best way to try to obtain better results is to employ a cool arc rather than by attempting to heat to a higher temperature and chill more suddenly.

The energy efficiency was not determined in these experiments. In later ones,[1] with a cooled arc, the efficiency, when the concentration of the nitric acid obtained was 3.4 percent, was 57 grams of nitric acid per kilowatt-hour, or 500 kilograms per kilowatt-year of 365×24 hours. With a cooled arc and a direct current, Holweg and Koenig[2] obtained nitric acid at a concentration of 2.5 percent and an efficiency corresponding to 80 grams of nitric acid per kilowatt-hour, the most favorable energy efficiency reached. Increasing the pressure above atmospheric does not increase this efficiency.[3]

On cooling down, the colorless nitric oxide changes to the brown dioxide of nitrogen, since the reversible reaction

$$NO + \tfrac{1}{2} O_2 \rightleftarrows NO_2$$
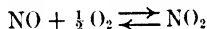
is displaced from left to right on cooling.

Table 59 shows how the dissociation of nitrogen dioxide is affected by the temperature :[4]

TABLE 59

DEGREES CENTIGRADE	PRESSURE IN CENTIMETERS	PERCENT OF NO_2 DECOMPOSED
130	71.85	
184	75.46	5.0
279	73.72	13.0
494	74.25	56.5
620	76.00	100.0

It will be interesting to compute from a purely thermal standpoint the energy necessary to produce nitric acid and to compare

[1] Z. f. Elektroch. **16**, 795 (1910).
[2] Z. f. Elektroch. **16**, 809 (1910)
[3] Haber and Holweg, Z. f. Elektroch **16**, 810 (1910).
[4] Nernst, *Theoretische Chemie*, 8–10 ed., p. 526. See also Bodenstein und Katayama, Z. f. Elektroch **15**, 244 (1909).

this result with those actually found by different experimenters. Assuming the temperature of the high tension arc to be 4200° C., the calculation is as follows.[1] From the equation given above at this temperature

$$\frac{p_{NO}}{p^{\frac{1}{2}}_{O_2} \cdot p^{\frac{1}{2}}_{N_2}} = 0.29,$$

and if the original mixture is air, the final composition is:

NO	O_2	N_2
10 percent	16 percent	74 percent

Ten mols of nitric oxide with air and water yield 630 grams of nitric acid. Therefore, in order to get this amount of acid, 100 mols must be heated to 4200° C., besides which $10 \times 21,600$ calories must be supplied for the reaction. Assuming the specific heat of the permanent gases to be $6.8 + 0.0006$ calories per mol, the total energy will be:

$$100(6.8 + 0.0006 \times 4200)4200 + 216,000 = 4,130,000 \text{ calories.}$$

This corresponds to 4.71 kilowatt-hours for 630 grams of nitric acid, or 134 grams per kilowatt-hour. If the arc were 1000° lower, the result would be 93.5 grams per kilowatt-hour.

The results obtained with a cooled arc are not due to thermal equilibrium, and of course have no relation to this calculation. Whether nitric oxide produced in the spark or in the high-tension arc is due to the thermal or to the electrical effect is an open question. The concentrations of nitric oxide produced is not too high to be due to the thermal effect alone. This concentration may, of course, be reached from a higher concentration of nitric oxide produced by the electrical effect, and then decomposed by the thermal effect. Even in this case the final concentration is due eventually to the thermal effect.

Lord Rayleigh[2] obtained an absorption of 21 liters an hour with 0.8 kilowatt, using a mixture of 9 parts of air and 11 of oxygen. This corresponds to 46 grams of pure nitric acid per kilowatt-hour, assuming the gas was measured at 20° C. and at atmospheric pressure. McDougall and Howles[3] with an arrangement similar to that of Lord Rayleigh obtained 33.5 grams of nitric acid per

[1] Haber, *Thermodynamics of Technical Gas Reactions*, p. 268.

[2] Journ. Chem. Soc. **71**, 181 (1897).

[3] Memoirs and Proceedings of the Manchester Literary and Phil. Soc. (IV), **44**, 1900, No. 13.

kilowatt-hour. McDougall and Howles were the first to make a small experimental plant for the production of nitric acid from the air.[1] It seems not to have got beyond the experimental stage, however.

The first[2] attempt to carry out the oxidation of nitrogen on a commercial scale was that of the Atmospheric Products Company
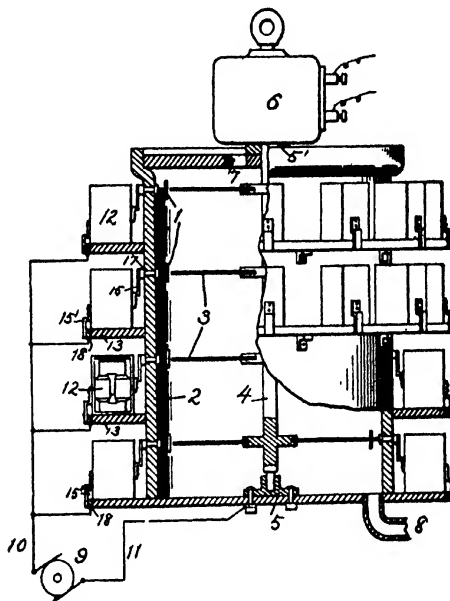
FIG. 202. — VERTICAL SECTION OF THE BRADLEY-LOVEJOY APPARATUS FOR OXIDIZING NITROGEN

at Niagara Falls, using the patents of Bradley and Lovejoy. Their final apparatus is shown in Figures 202 and 203.[3] This consisted in an iron cylinder 5 feet high, 4 feet in diameter, in the center of which was a rotating shaft carrying a series of radial arms, the ends of which were tipped with platinum. Six rows of 23 inlet wires

[1] Huber, *Zur Stickstoff Frage*, p. 41, Bern (1908).

[2] Donath and Frenzel, *Die Technische Ausnutzung des Atmosphärischen Stickstoffes*, p. 117 (1907).

[3] J. W. Richards, Electroch. Ind. **1**, 20 (1902); U. S. Pat. 709,868 (1902).

projected through the cylinder and terminated in platinum hooks. As the radial arms rotated, their platinum tips passed the hooks on the inlet wires, coming within one millimeter of touching at the nearest point. An arc was formed which was drawn out from 4 to 6 inches before going out. The arms were so arranged that the arcs between them and the inlet wires were formed successively rather than simultaneously. The central shaft made 500 rotations per minute, and formed 6900 sparks a second. Each inlet wire had in series with it an induction coil 12 inches long and 5 inches in diameter, wound with very fine wire and immersed in
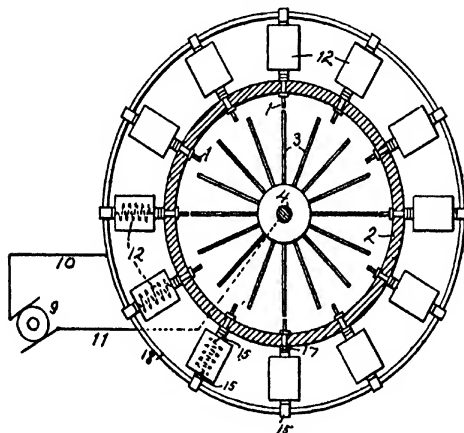
FIG. 203. — HORIZONTAL SECTION OF THE BRADLEY-LOVEJOY APPARATUS FOR OXIDIZING NITROGEN

oil. The self-induction of the coil caused the spark to be drawn out to a greater length than would be possible without induction. A direct-current generator was especially designed for this plant, giving 8000 volts and 0.75 ampere. Air passed in at the rate of 11.3 cubic meters per second and came out of the cylinder containing 2.5 percent nitric oxide.[1] The yield is said to have been one pound of acid per 7 horse-power-hours, or 87 grams per kilowatt-hour. The process was not successful, however, and the company was forced to give up the experiments in 1904. Though the yield compared favorably with the calculations given above, the apparatus was very complicated and subject to considerable

[1] Haber, Z. f. Elektroch. **9**, 381 (1903).

wear. The iron drum corroded rapidly in spite of the inside coating of asphalt paint.

The first successful process for oxidizing nitrogen on a commercial scale is that of Birkeland and Eyde. A factory for carrying it out was started at Notodden, Norway, in May, 1905.[1] The high voltage flame is formed between two electrodes consisting of water-cooled copper tubes 1.5 centimeters in diameter with 0.8 centimeter between the ends. An alternating current of 50 cycles per second is supplied to the electrodes at 5000 volts. In order to spread the flame over a large area an electromagnet is placed at right angles to the electrodes so that the terminals lie between the
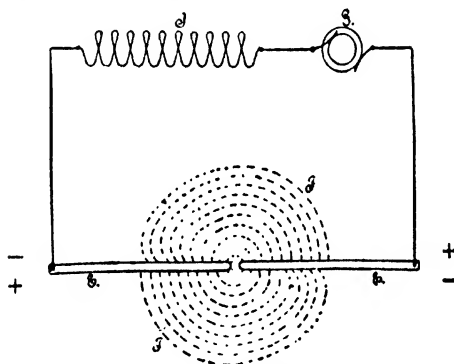
FIG. 204 — THE BIRKELAND-EYDE ARC

poles of the magnet. The voltage is sufficiently high to cause the flame to form of itself between the electrodes at their nearest points, whereupon the magnetic field causes the ends of the flame to travel along the electrodes until the current is reversed. A new flame is then started on the other side of the electrodes. When the furnace is running properly a flame is formed at each reversal of the current every $\frac{1}{50}$ of a second, though if the distance between the electrodes is too short or the magnetic field too strong, several hundred flames may be started during one period. The magnetic field is 4000 to 5000 lines per square centimeter at the center. The result of this combination is an electric disk flame, as shown in Figure 204. This is inclosed in a narrow iron furnace lined with firebrick, forming a chamber from 5 to 15 centimeters wide, shown

[1] Birkeland, Tr. Faraday Soc. **2**, 98 (1906).

in Figure 205. Air passes in through the walls and leaves the furnace at a temperature of 1000° C., containing one percent of nitric oxide.[1] From the furnace the gases pass through a steam boiler in which they are cooled to 200° C., and then through a cooling apparatus in which their temperature is reduced to 50° C. They then enter oxidation chambers with acid-proof lining, where the reaction $NO + \frac{1}{2}O_2 = NO_2$ is completed.

The next step is to absorb the nitrogen dioxide. This is done in two sets of five stone towers whose inside dimensions are $2 \times 2 \times 10$ meters. The first four towers are filled with broken quartz over which water trickles. The liquid from the fourth tower is raised by compressed air to the top of the third, that from the third to the top of the second, and so on until 30 percent nitric acid is formed at the bottom of the first tower. This is concentrated to 98 percent and put into aluminum containers. These towers recover 80 percent of the nitric oxide; in order to get 15 percent more the gas from the fourth tower passes through a fifth, where it is absorbed by sodium hydrate. Some nitric acid is changed to calcium nitrate by passing through open towers filled with limestone. Some of this acid is used to decompose the nitrate-nitrite mixture from the fifth tower. The nitric oxide thereby evolved is sent into the absorbing system again. The yield is 62.5 grams of pure nitric acid per kilowatt-hour.

In a 1600-kilowatt furnace at about 5000 volts the disk flame has a diameter of 2 meters and a thickness of 10 centimeters.[2]

FIG. 205. — VERTICAL SECTION OF THE BIRKELAND-EYDE FURNACE

[1] Hagemann, Chem. Met. Eng. **24**, 531 (1921); **29**, 502 (1923). See also, Eyde, Electroch. Met. Ind. **7**, 306 (1909); Lof, Gen. El. Rev. **26**, 136 (1923).

[2] Birkeland, Electroch. Met. Ind. **7**, 305 (1909).
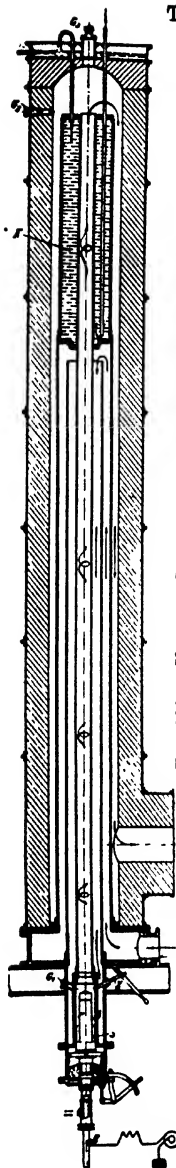
FIG. 206. — VERTICAL SECTION OF THE SCHÖNHERR-HESSBERGER FURNACE

Furnaces taking 4000 kilowatts are now built.[1] The power cost is half the total expense of running this process. In Norway the total cost is 1780 kr. ($476, exchange at par) per 1000 kilograms of fixed nitrogen. These figures apply also to the two arc processes described below.

The furnace of the Badische Anilin- und Sodafabrik of Ludwigshafen, Germany, was invented in 1905 by Schönherr and Hessberger.[2] An alternating-current arc is very easily extinguished, especially if air is blown across it. The principle underlying this furnace is that an alternating-current arc loses its unstable character and becomes as quiet as a candle if a current of air is passed around it in a helical path. With this method of air circulation the arc may be included in a metallic tube without risk of its coming in contact with the sides of the tube. A cross-section of the apparatus is shown in Figure 206. It consists of a number of concentric vertical iron tubes. The electrode at the bottom is an iron rod adjustable within a water-cooled copper cylinder. The iron is slowly eaten away, and is fed in at about the rate of one electrode in three months. The electrode Z is for starting the arc by bringing it in contact with E. There is, of course, an induction coil in series with the arc to make it steady and prevent the current from being too large on starting. When Z is drawn back, the arc is formed between E and the walls of the tube. The air then drives it up along the tube until it reaches the other water-cooled end, K, within which the arc terminates. G_1, G_2, and G_3 are peep-holes for observing the

[1] Creighton, J. Franklin Inst. **187**, 386 (1919).
[2] Electroch. Met. Ind. **7**, 245 (1909); Tr. Am. Electroch. Soc. **16**, 131 (1909).

ends of the arc. In the 447-kilowatt furnaces at Kristians-
sand, Norway, the arc is 5 meters long, and 7 meters in the 746-
kilowatt furnaces. The circulation of the air is evident from
the figure.

Fig. 207. — Schönherr-Hessberger Furnaces at Kristianssand

The capacity of this type of furnace is said to be limited to
1000 kilowatts. When the arc is extinguished, which frequently
happens, it must be started by hand.[1]

The plant at Kristianssand, the furnace room of which is shown
in Figure 207, has been in operation since the autumn of 1907.
Three-phase currents are used, and the furnaces are connected

[1] Creighton, J. Franklin Inst. **187**, 391 (1919).

in star. The power factor varies between 0.93 and 0.96. It is estimated that 3 percent of the power is used in the formation of nitric oxide, 40 percent is recovered in the form of hot water, 17 percent is lost by radiation, 30 percent is used in the steam boiler, and 10 percent is removed by water cooling after the gases have passed the steam boiler.

·A third process for the fixation of atmospheric nitrogen, invented by H. and G. Pauling, is carried out near Innsbruck, Tyrol, by the "Salpetersäure-Industrie-Gesellschaft."[1] The arcs are produced between curved electrodes, as shown in Figure 208. The arc is lighted where the electrodes are nearest together, is blown upward by the hot air rising between the electrodes, and is broken every half period of the alternating current. Another arc is then formed, and so on. In Figure 208, c represents two thin adjustable blades for starting the arc. Air is blown in through the tube c. The electrodes are iron pipes,[2] water-cooled
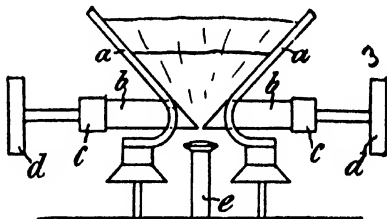
FIG. 208 — SECTION OF PAULING FURNACE

and separated by about 4 centimeters at their nearest point. Their life is about 200 hours. With a 400-kilowatt furnace of 4000 volts the length of the flame is about one meter. These furnaces are built to absorb up to 1000 kilowatts at 6000 volts. Cooling is produced by passing cold air into the upper part of the flame from the side. The concentration of the nitric oxide is about 1.5 percent. The furnaces used have two arcs in series. Six hundred cubic meters of air per hour pass through the furnace, excluding the cooling air. The yield is 60 grams of nitric acid per kilowatt-hour. At present there are 24 furnaces in operation at Innsbruck, having a capacity of 15,000 horse power. The products are nitric acid and sodium nitrite. This process was also used temporarily at Great Falls, South Carolina, by the Southern Electrochemical Company.

A number of other furnaces for the oxidation of nitrogen have

[1] Electroch. Met. Ind. 7, 430 (1909).
[2] Rossi has found that aluminum electrodes give better yields than iron, on account of the decomposing action of iron oxide on nitric oxide. Partington and Parker, *The Nitrogen Industry*, p. 239 (1923).

been invented, but their descriptions are omitted here because they are not in operation on a commercial scale.

The chief advantages of the arc process are the direct production of nitric acid, free raw materials, small labor requirements, and possibility of operating with off-peak power. The disadvantages are the large power requirement and high installation cost.[1]

The Synthesis of Ammonia. — The third method of combining nitrogen is to form ammonia by the reaction:

$$\tfrac{1}{2} N_2 + \tfrac{3}{2} H_2 \rightleftarrows NH_3 + 10950 \text{ cal.}$$
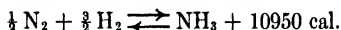
The equilibrium concentrations of ammonia in nitrogen-hydrogen mixture are given in Table 60.[2]

TABLE 60. PERCENT AMMONIA IN EQUILIBRIUM WITH NITROGEN-HYDROGEN MIXTURE (3 VOL. H_2 + 1 VOL. N_2)

Deg. C.	$\dfrac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} \cdot p_{H_2}^{\frac{3}{2}}}$	VOLUME PERCENT AMMONIA IN EQUILIBRIUM MIXTURE AT					
		1 at.	30 at.	100 at.	200 at.	1000 at.[3]	
						Temp.	Percent NH₃
200	0.660	15.3	67.6	80.6	85.8	536°	41
300	0.070	2.18	31.8	52.1	62.8	607	30
400	0.0138	0.44	10.7	25.1	36.3	672	20
500	0.0040	0.210	3.6	10.4	17.6	740	14
600	0.00151	0.049	1.43	4.47	8.25		
700	0.00069	0.0223	0.66	2.14	4.11		
800	0.00036	0.0117	0.35	1.15	2.24		
900	0.000212	0.0069	0.21	0.68	1.34		
1000	0.000136	0.0044	0.13	0.44	0.87		

According to some experiments of Maxted,[4] the equilibrium concentration of ammonia passes through a minimum between 1000° and 1500° C. and increases at higher temperatures. This would mean that the heat of the reaction changes sign, which is not probable. The temperatures were only estimated, not measured, which may account for the results.

The ammonia equilibrium has been the subject of numerous researches, but its technical development is largely due to the work of Haber, which began in 1905. It was taken up by the Badische Anilin- und Sodafabrik and worked out at Oppau after years of

[1] Creighton, J. Frank'in Inst. **187**, 391 (1919).
[2] Haber, Z. Elektroch. **20**, 603 (1914).
[3] Claude, Chem. Ztg. **44**, 592 (1920).
[4] J. Soc. Chem. Ind. **37**, 232 (1918).

experimenting.[1] The problems which had to be solved were: (1) the production of large quantities of very pure nitrogen and hydrogen, (2) extraction of ammonia from the mixture, (3) conversion of ammonia into other products, and (4) the design and construction of suitable apparatus.

The nitrogen-hydrogen mixture is obtained by mixing water gas, $CO + H_2$, with producer gas, $CO + xN_2$, and with steam, and passing this mixture over a catalyzer between 400° and 500° C. The reaction $CO + H_2O = H_2 + CO_2$ takes place and the carbon dioxide is dissolved in water under pressure. The residue of carbon monoxide is removed by an ammoniacal solution of copper formate, the dioxide, by caustic soda. The composition of the mixture is then adjusted to exactly three volumes of hydrogen to one of nitrogen by adding pure nitrogen from liquid air. This mixture is passed through the reaction chamber containing the catalyzer at about 500° C. and 200 atmospheres pressure. The ammonia produced is absorbed in water, or is liquefied, and the mixture is circulated again through the reaction chamber, where it does not remain long enough to reach equilibrium, as more ammonia can be made in a given time by circulating the mixture more rapidly. Usually the mixture leaving the reaction chamber contains 5 percent of ammonia. Part is oxidized to nitric acid and a part changed to ammonium sulfate, nitrate, and chloride. The Oppau plant cost $75,000,000 and had a yearly production of 300 tons of ammonia. The plant at Mercersburg is said to have a capacity of 900 tons. The cost of combined nitrogen by this process at pre-war prices is estimated at 0.70 mark per kilogram.

The catalyzers are principally reduced iron mixed with various *promoters*, substances which increase the activity of a catalyzer, such as oxides of alkali metals, and they are very sensitive to impurities. Other catalyzers are osmium, uranium carbide, tungsten, and molybdenum. Small amounts of carbon dioxide, oxygen, and moisture decrease their activities.

The bombs in which the reaction takes place must be of carbon-free chrome steel, for hydrogen at high temperature removes carbon from steel and weakens it. At Oppau the bombs were 12 m. long and 1.1 m. in external diameter. The walls were 12 cm. thick.

By proper design of the apparatus, the heat evolved by the reaction can be made to offset the heat losses. The supply of additional heat is said to be a serious problem.

[1] Chem. Met. Eng. **24**, 305 (1921); Tour, J. Ind. Eng. Ch. **12**, 844 (1920), and series of articles in Chem. Met. Eng. **26** (1922).

The government plant at Sheffield, Alabama, known as Nitrat
Plant No. 1, is designed to work at 100 atmospheres and to remov:
the ammonia by liquefaction.   This plant is not now in operation
but a plant of the Atmospheric Nitrogen Company, at Syracuse
is in operation, using 100 atmospheres pressure.

The Claude process[1] employs the same reaction as the Haber
process but the pressure at which the gases react is 1000 atmos-
pheres, which gives 25 percent conversion, while the Haber process
gives 6 percent.   The temperature is about 500° C. and a catalyzer
is required.   It is said that a serious objection to this high pressure
is the resulting short life of the apparatus.

Other Nitrogen-Fixation Processes.—Besides the three methods
of fixing atmospheric nitrogen described above, there are a number
of others not yet fully developed.   Among the most important of
these are the *Bucher* and the *Serpek* processes.

In the Serpek process[2] aluminum nitride is made from bauxite
according to the reaction :

$$Al_2O_3 + 3 C + N_2 = 2 AlN + 3 CO - 213,220 \text{ cal.}$$

According to Tucker and Read[3] this reaction takes place to a very
slight extent below 1600° C., while the maximum amount of com-
bined nitrogen is obtained between 1800° and 2000° C.   Above
2000° the nitride decomposes.   Petroleum coke was used in these
experiments.   With lampblack Fraenkel[4] found the reaction
begins below 1400° and becomes rapid above 1500° C.   He also
found that the reaction is reversible, depending on the relative
amounts of nitrogen and carbon monoxide.   If the nitrogen is
diluted with carbon monoxide, a higher temperature is required to
make the reaction go from left to right.

The plant devised by Serpek for carrying out this reaction
consists of two rotating, cylindrical kilns, placed as shown in
Figure 209.   Bauxite enters the upper kiln, where it is calcined.
At *m* it is mixed with the necessary carbon and this mixture then
passes to the lower kiln, where it is treated with nitrogen at a
temperature between 1800° and 1900° C.   Heating takes place in
a detachable electric resistance furnace *f*, consisting of compressed
carbon disks, which cross the furnace diametrically and are ar-

[1] Chem. Met. Eng. **23**, 22 and 395 (1920); **28**, 498 (1923).
[2] Richards, Tr. Am. Electroch. Soc. **23**, 351 (1913); U. S. Pat. **996,032**
(1911).
[3] Tr. Am. Electroch. Soc. **22**, 57 (1913).
[4] Z. f. Elektroch. **19**, 362 (1913); **22**, 107 (1916).
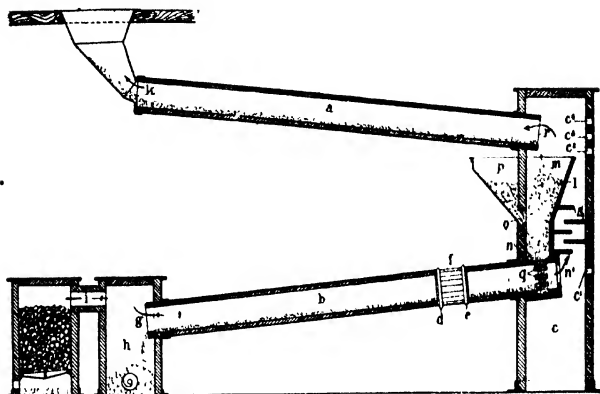
Fig. 209. — Section of the Serpek Apparatus for Fixing Nitrogen

ranged in eight columns each 1.2 meters long, connected in series. A direct current of 10,000 amperes at 230 volts is used.[1] The treated material is discharged into an airtight receiver. Producer gas ($\frac{1}{3}$ CO + $\frac{2}{3}$ N$_2$) enters the lower end of the lower kiln and is preheated by the descending charge. After passing through the furnace it is enriched by the reaction in carbon monoxide and in passing the upper part of the kiln preheats the descending charge. The gas then enters a vertical chamber c with baffle plates, where silica and other impurities are condensed. On entering the lower end of the second kiln a the gas meets a blast of air which burns it for heating the bauxite as it passes through the upper tube.

On treating aluminum nitride with dilute alkali solution, the following reaction takes place:

$$\text{AlN} + 3\,\text{H}_2\text{O} = \text{Al(OH)}_3 + \text{NH}_3.$$
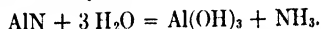
The alumina produced is very pure and the financial success of the process depends on using this by-product for the manufacture of aluminum.

The endothermic reaction alone absorbs one kilowatt-day per 2.7 kilograms of fixed nitrogen. In practice at least twice this energy would be required, so that one kilowatt-day would not fix more than 1.3 kilograms of nitrogen.

One advantage of this process is that impure nitrogen can be used.

[1] Creighton, J. Franklin Inst. **187**, 608 (1919).

The Bucher process uses the following reaction:

$$Na_2CO_3 + 4\,C + N_2 = 2\,NaCN + 3\,CO - 138,500 \text{ cal.};$$
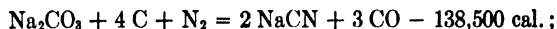
it proceeds rapidly in the neighborhood of 1000° C. in the presence of finely divided iron as catalyzer. This reaction was discovered by Lewis Thompson in 1839, was tried on a commercial scale, and was given up. This failure Bucher attributes to leaving iron out of the mixture, though its presence was stated by the original inventor to be necessary.[1] In recent years Bucher's extensive investigations have revived interest in the process.

Bucher's method of preparing the material for treatment with nitrogen consists in mixing soda ash, carbon powder, and iron with water at a temperature above that at which soda ash loses part of its water of crystallization. This hot paste is briquetted by forcing through a meat chopper of the disk type, giving briquettes $\frac{5}{16}$ inch in diameter and of variable length. These are dried with the exclusion of air, and are then ready for nitrifying.

The extent to which sodium is converted to cyanide depends on the temperature and the quantity of carbon monoxide in the nitrogen, as shown by the graphs in Figure 210.[2] The reaction takes place rapidly and is usually completed in an hour. Any kind of carbon free from ash, such as lampblack, petroleum coke, gascarbon, or charcoal, gives good results.[3] In order to get the best results the iron should be finely
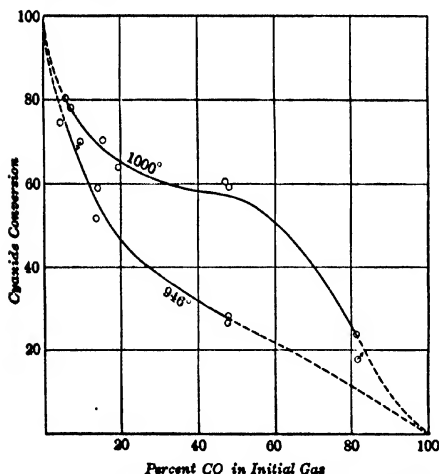
Fig. 210. — Graphs of the Conversion of Sodium Carbonate to Cyanide by Nitrogen Containing Carbon Monoxide

[1] J. Ind. Eng. Ch. 9, 233 (1917).
[2] Ferguson and Manning, J. Ind. Eng. Ch. 11, 946 (1919).
[3] Thompson, Chem. Met. Eng. 26, 124 (1922).

divided by precipitation, and it is then possible to make briquettes in which over 90 percent of the sodium is in the form of cyanide.[1]

If briquettes are made with a sufficiently large proportion of soda ash, they remain hard after treatment; if not, they are soft and fall to pieces on handling.

During the war the government built a plant at Saltville, Virginia, for carrying out this process.[2] The briquettes were passed through ferrochromium tubes 9 inches in diameter, heated by gas. The cyanide was leached with liquid ammonia, which does not dissolve the other sodium salts present. The armistice was declared before this plant was ever run at full capacity.

This reaction requires careful heat control and therefore should be heated electrically. The briquettes do not conduct well when cold, but are good conductors at 1000° C. It is important to heat the whole charge to the cyaniding temperature, for if part is below this temperature the sodium carbonate gives off carbonic acid slowly and thus prevents the briquettes at the high temperature from reaching a high concentration of cyanide.

Raw materials and power would cost about six cents per pound of sodium cyanide.

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[1] Thompson, Chem. Met. Eng **26**, 124 (1922).
[2] Brown, J. Ind. Eng. Ch. **11**, 1010 (1919).

CHAPTER XXI

THE PRODUCTION OF OZONE

General Discussion. — In 1785 van Marum observed that oxygen through which an electric spark had passed had a peculiar odor, and that it at once tarnished a bright surface of mercury.[1] Nothing was done to throw light on this phenomenon until 1840, when it was investigated by Schönbein. He had observed for a number of years previously that during the electrolysis of aqueous solutions an odor is produced in the gas evolved at the anode similar to that resulting from the discharge of electricity from points.[2] He described a number of the properties of this substance, and suggested the name ozone, from ὄζων, meaning *smelling*. For many years the chemical nature of this oxidizing principle was unknown, but it was found eventually, after a great number of investigations, to be simply condensed oxygen with the formula O_3.

The formation of ozone from oxygen is an endothermic reaction:

$$\tfrac{3}{2} O_2 = O_3 - 34,000 \text{ cal. and } \Delta F = - 32,400 \text{ cal.}[3]$$
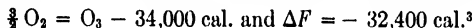
Since heat is absorbed in the production of ozone, thermodynamics requires that the equilibrium existing in a mixture of oxygen and ozone be displaced in the direction of a greater ozone concentration by an increase in the temperature of the mixture. In order to prove this experimentally, it is necessary to heat the oxygen to a temperature high enough to produce a measurable quantity of ozone, and then, by cooling suddenly, to prevent the decomposition of the ozone formed. This has been done by blowing air or oxygen against a hot pencil, such as is used in a Nernst lamp,[4] and also by dipping a hot Nernst pencil, or hot platinum, in liquid air.[5]

[1] Roscoe and Schorlemmer, *Treatise on Chemistry*, **1**, 262 (1920).
[2] Pogg. Ann. **50**, 616 (1840).
[3] Lewis and Randall, *Thermodynamics*, p. 476 (1923).
[4] Fischer and Marx, B. B. **40**, 443 (1907).
[5] Fischer and Braehmer, B. B. **39**, 940 (1906).

Ozone may also be produced by the action of ultra-violet light, and of the brush discharge of electricity on oxygen and by electrolysis. While the brush electric discharge is the only method used commercially for the manufacture of ozone, it will be interesting to compare the yield per kilowatt-hour attained by the brush discharge with some of the other methods. By blowing air against a' hot Nernst pencil, the yield was found to be one gram per kilowatt-hour; and by dipping hot bodies in liquid air, about 3.5 grams. The concentration of the ozone in both cases was less than three percent. By electrolyzing solutions of sulfuric acid of specific gravity between 1.075 and 1.1 with a water-cooled platinum anode, at 13° C. and a current density of 5800 amp./sq. dm. 23 percent by weight of the oxygen given off at the anode has been obtained in the form of ozone and 28 percent at − 14° C. The best energy yield was 7.18 g./kw.-hr. at 7.8 volts.[1]

When compared with 70 grams per kilowatt-hour, the yield obtained with the brush discharge, these methods are seen to be inefficient from an economical standpoint, though if a high concentration is desired, this can be best obtained by electrolysis.

In most of the theoretical work done on the formation of ozone by the brush discharge, there was no dielectric between the electrodes, and it is therefore not directly applicable to commercial ozonizers, which nearly always have a dielectric. Moreover, no general laws have been discovered, and different experimenters do not agree even as to facts. For example, Warburg[2] finds that the negative brush produces a greater concentration of ozone than the positive, while in the work done at the Mellon Institute for the United States Ozone Company, the contrary was found.[3] Vosmaer apparently also considers the positive brush the more effective.[4] For these reasons it does not seem worth while to summarize the effects of the different conditions on the ampere-hour and watt-hour yields. All that it is necessary to remember is that in the production of ozone by the brush discharge, an equilibrium is reached which depends on the conditions of the experiment, such as the pressure, temperature, moisture content of the air or oxygen, the shape, size, and distance apart, finish, and age of the electrodes, whether the current is alternating or direct, and if alternating, its frequency and wave form. With high frequency

[1] Fischer and Massenez, Z. f. anorg. Ch. 52, 202 and 229 (1907).
[2] Ann. d. Phys. 9, 781 (1902); 17, 1 (1905); 28, 17 (1909).
[3] Hartman, The Truth about Ozone, p. 59 (1922).
[4] Ozone, p. 45 (1916).

a greater amount of ozone can be produced per tube on account of the greater absorption of energy, but the energy yield and the concentration of ozone obtainable are not increased. This is shown in Tables 61 and 62.[1]

The energy efficiency of industrial ozonizers is only about 5 percent in air and 15 percent in oxygen.

TABLE 61.[2] PRODUCTION OF OZONE WITH HIGH-FREQUENCY UNDAMPED WAVES

Frequency	Absorption of Energy of the Tube, W.	Energy Yield, G./Kw.	Ozone Concentration, G./Cu. M.	Ozone Yield per Tube per Hour, G.	Tension, V.	Nature of Gas
50	2.12	134	21.3	0.285	5480	Oxygen
480	22.07	135	21.1	2.98	5830	Oxygen
770	31.9	135	22.5	4.31	5850	Oxygen
1,080	44.2	130	23.0	5.73	5850	Oxygen
2,510	118.7	138	20.7	16.4	5850	Oxygen
4,810	207.0	138	22.7	28.6	5850	Oxygen
6,880	303.0	146	20.5	44.5	5850	Oxygen
7,900	348.0	142	19.7	49.4	5850	Oxygen
10,020	415.0	139	22.6	57.7	5830	Oxygen

TABLE 62.[2] PRODUCTION OF OZONE WITH HIGH-FREQUENCY UNDAMPED WAVE

Frequency	Absorption of Energy of the Tube, W.	Energy Yield, G./Kw.	Ozone Concentration, G./Cu M	Ozone Yield per Tube per Hour, G	Tension, V.	Nature of the Gas
50	1.97	48	6.3	0.095	5830	Air
410	16.3	51	6.1	0.831	5830	Air
980	41.5	46	5.9	1.91	5850	Air
1,910	82.7	49	6.2	4.06	5840	Air
2,780	119.8	50	5.7	5.98	5840	Air
3,520	152.1	53	6.4	8.06	5850	Air
4,650	198.0	48	5.3	9.50	5850	Air
5,260	219.0	47	6.0	10.30	5830	Air
6,010	248.0	51	6.2	12.65	5850	Air
6,970	284.0	49	5.8	13.91	5850	Air
7,930	315.0	47	6.4	14.80	5850	Air
8,980	350.0	52	6.1	18.20	5850	Air
10,030	389.0	49	5.8	19.10	5850	Air

[1] Hartman, Tr. Am. Electroch. Soc. **44**, 227 (1923). See also Starke, Z. f. Elektroch. **29**, 358 (1923).
[2] Reproduced from Dr. Alfred Starke's thesis (1922).

In technical ozonizers no attempt is made to reach equilibrium, because at this point the energy efficiency is zero, and is the higher the farther the concentration is from equilibrium. Thus if air is passed through an ozonizer slowly, the concentration of ozone will be relatively high, but the energy yield low.

The air is always dried, usually by refrigeration or by calcium chloride.

The Technical Production of Ozone. — Ozone is produced commercially for the purification of water, for bleaching wax, textiles, paper pulp, and sponges; for drying varnishes and paint; for deodorizing cold-storage chambers, and for use as an oxidizing agent in organic chemistry.[1]

In water purification, the action of ozone is to oxidize the organic matter and to destroy germs.

Siemens and Halske make the ozone apparatus shown in Figure 211.[2] The discharge chamber is between two concentric metal cylinders, between which 8000 volts alternating are applied.

FIG. 211. — SIEMENS AND HALSKE OZONIZER

The cylinders are immersed in water for cooling, and the outer one is connected to earth. One of the surfaces from which the discharge takes place is covered with a glass dielectric. Air enters at the top, is partly changed to ozone in passing between the walls of the concentric cylinders, and leaves the apparatus from below. The concentration of the ozone is about 2 grams per cubic meter, which is high enough for
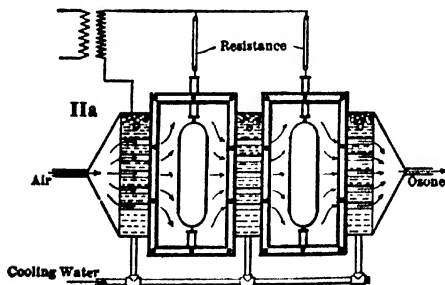
FIG. 212. — TINDAL OZONIZER

[1] J. W. Swan, Z. f. Elektroch. **7**, 950 (1901); *Ozone*, E. K. Rideal, p. 142 (1920); Jones, Chem. Met. Eng. **22**, 805 (1920).

[2] Z. f. Elektroch. **10**, 13 (1904); Electroch. Ind. **2**, 67 (1904).
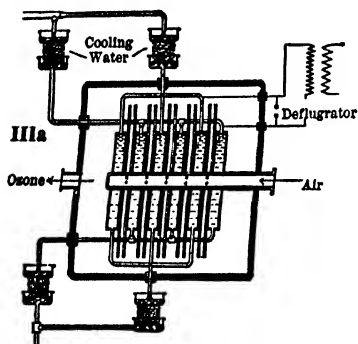
FIG. 213. — ABRAHAM-MARMIER OZONIZER

all ordinary purposes. The yield varies between 18 and 37 grams per kilowatt-hour.[1]

The Tindal ozonizer is shown in Figure 212. It is in the form of a box, the inner walls of which are water-cooled electrodes and are connected to earth. The other electrodes are metal plates inside the box and insulated from it. Between 40,000 and 50,000 volts are applied to the electrodes. There is no dielectric.

The Abraham-Marmier apparatus is shown in Figure 213. It consists of a number of cylindrical, parallel, hollow electrodes of about a square meter area, covered with glass and mounted in a box. Water circulates through the electrodes for cooling, between which about 40,000 volts are applied.

The Otto apparatus[2] is shown in Figures 214 and 215. It consists

FIG. 214. — LONGITUDINAL-VERTICAL SECTION OF THE OTTO OZONIZER

of a chamber, K, the metal wall, E_1, of which forms one electrode.

FIG. 215. — TRANSVERSE-VERTICAL SECTION OF THE OTTO OZONIZER

The sheet steel rings, S, sharpened at M, and mounted on an axle on which they rotate, are the other electrode, E. There is no solid dielectric. Air passes in the box at B and comes out at A. While in the box it is ozonized and thoroughly mixed by the rotating electrode. If an arc were to form between the electrodes, it would be extinguished as the grooves RR in the rotating electrode pass the insulating base of the box, aa. About 20,000 volts are applied to the electrodes, the distance between which may be from 10 to 1000 millimeters. The frequency is 500, and the yield is 40 g./kw.-hr.

[1] Askenasy, *Technische Elektrochemie*, **1**, 246 (1910).
[2] Z. f. Elektroch. **7**, 790 (1901).

The Vosmaer ozonizer [1] is shown in Figure 216, in horizontal and in vertical section. The strips *a* are the sharp-edged electrodes, *b* the air spaces, *c* the dielectrics, and *d* the flat poles. About 10,000 volts are applied to the plates. At the usual concentration of one gram of ozone per cubic meter the yield is 50 g./kw.-hr. The units are made from 100 to 1000 watts.

The ozonizer made by the United States Ozone Company, of Scottdale, Pa., consists of an aluminum plate placed between two sheets of dielectric, consisting of mica flake of special size put together with a binder whose composition is not disclosed, with an air space between the plate and the dielectric. The casing is aluminum and acts as the other electrode. Figure 217 shows two generators and the electric connections. Radiation fins are placed all over the outer surface of the casing for cooling, which

FIG. 216. — THE VOSMAER OZONIZER: VERTICAL SECTION ABOVE HORIZONTAL SECTION BELOW

prevent the temperature from rising more than 6° C. above room temperature, when working at the prescribed current density. The rheostat is for taking care of the variations in primary voltage of the 110 to 10,000 volt step-up transformer. The primary voltage should not vary more than 5 volts above or below the mean.

In case an arc forms, there is rarely more than a 25 percent increase in the current, which is too small to be protected by fuses. Therefore the overload relay is placed in the primary circuit, which opens in case an arc forms and remains open until closed by hand, after replacing the dielectric.

The life of the dielectric is almost indefinite when the air or oxygen is dry and the voltage does not vary more than six per-

[1] Reproduced from Vosmaer's *Ozone, Its Manufacture, Properties, and Uses*, p. 108 (1916). D Van Nostrand Company.

cent plus or minus, but when the gas has only ten percent relative humidity at 15° C. a dielectric will not last over a month. Dehydration on a large scale is best accomplished by refrigeration; calcium chloride is better for small scale.

About a thousand of these ozonizers are said to be in daily operation in the United States.
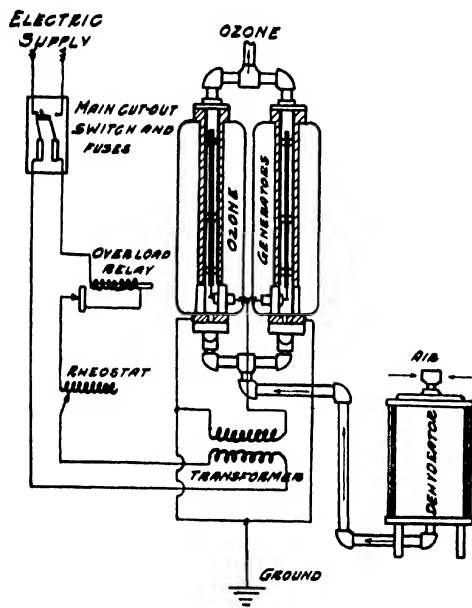
FIG. 217. — SECTION OF OZONIZERS AND ACCESSORIES OF THE UNITED STATES OZONE COMPANY

Figure 218 shows the relation between the concentration and the yield for these ozonizers.[1]

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[1] *The Truth about Ozone*, by F. E. Hartman, Technical Publication No. 14, United States Ozone Co.
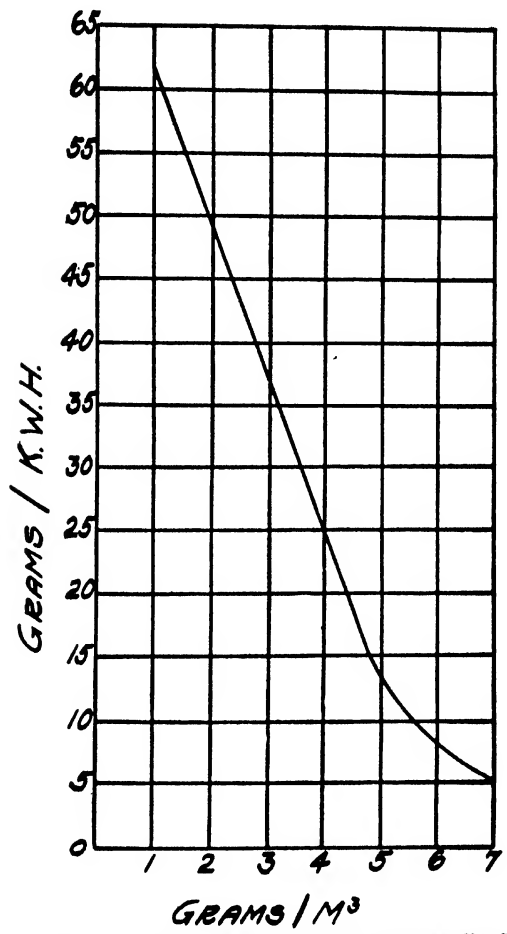
Fig. 218. — Graph Showing the Relation between Grams per Kw.-Hr. and Grams per Cb. M. of the United States Ozone Company's Ozonizer

APPENDIX

TABLE OF INTERNATIONAL ATOMIC WEIGHTS

$0 = 16.000$

			(1923) [1]				(1923)
Aluminum	. .	. Al	27.1	Iridium	. .	. Ir	193.1
Antimony	. .	. Sb	120.2	Iron	. . .	. Fe	55.84
Argon	. . .	. A	39.9	Krypton	. .	. Kr	82.92
Arsenic	. .	. As	74.96	Lanthanum	.	. La	139.0
Barium	. .	. Ba	137.37	Lead	. . .	. Pb	207.20
Bismuth	. .	. Bi	209.0	Lithium	. .	. Li	6.94
Boron	. .	. B	10.9	Lutecium	. .	. Lu	175.0
Bromine	. .	. Br	79.92	Magnesium	. .	. Mg	24.32
Cadmium	. .	. Cd	112.40	Manganese	. .	. Mn	54.93
Caesium	. .	. Cs	132.81	Mercury	. .	. Hg	200.6
Calcium	. .	. Ca	40.07	Molybdenum	.	. Mo	96.0
Carbon	. .	. C	12.005	Neodymium	.	. Nd	144.3
Cerium	. .	. Ce	140.25	Neon	. . .	. Ne	20.2
Chlorine	. .	. Cl	35.46	Nickel	. .	. Ni	58.68
Chromium	. .	. Cr	52.0	Niton	. .	. Nt	222.4
Cobalt	. .	. Co	58 97	Nitrogen	. .	. N	14.008
Columbium	.	. Cb	93.1	Osmium	.	. Os	190.9
Copper	. .	. Cu	63.57	Oxygen	. .	. O	16.000
Dysprosium	.	. Dy	162.5	Palladium	. .	. Pd	106.5
Erbium	. .	. Er	167.7	Phosphorus	.	. P	31.04
Europium	.	. Eu	152.0	Platinum	. .	. Pt	195.2
Fluorine	. .	. Fl	19.0	Potassium	. .	. K	39.10
Gadolinium	.	. Gd	157.3	Praseodymium		. Pr	140.9
Gallium	. .	. Ga	70.1	Radium	. .	. Rd	226.0
Germanium	.	. Ge	72.1	Rhodium	. .	. Rh	102.9
Glucinum	. .	. Gl	9.1	Rubidium	. .	. Rb	85.45
Gold	. . .	. Au	197.3	Ruthenium	. .	. Ru	101.7
Helium	. .	. He	4.00	Samarium	. .	. Sm	150.4
Holmium	. .	. Ho	163.5	Scandium	. .	. Sc	45.1
Hydrogen	. .	. H	1.008	Selenium	. .	. Se	79.2
Indium	. .	. In	114.8	Silicon	. .	. Si	28.1
Iodine	. .	. I	126.92	Silver	. .	. Ag	107.88

[1] International Committee on Atomic Weights, J. Am. Chem. Soc. **43**, 1751 (1921); **44**, 427 (1922); **45**, 867 (1923).

TABLE OF INTERNATIONAL ATOMIC WEIGHTS — *Continued*

		(1923)			(1923)
Sodium	. . . . Na	23.00	Titanium	. . . Ti	48.1
Strontium	. . . Sr	87.63	Tungsten	. . . W	184.0
Sulfur	. . . . S	32.06	Uranium	. . . . U	238.2
Tantalum	. . . Ta	181.5	Vanadium	. . . V	51.0
Tellurium	. . . Te	127.5	Xenon	. . . . Xe	130.2
Terbium	. . . Tb	159.2	Ytterbium	. . . Yb	173.5
Thallium	. . . Tl	204.0	Yttrium	. . . . Y	89.33
Thorium	. . . . Th	232.15	Zinc	. . . . . Zn	65.37
Thulium	. . . . Tm	169.9	Zirconium	. . . Zr	90.6
Tin	. . . . . Sn	118.7			

TABLE OF ELECTROCHEMICAL EQUIVALENTS OF THE MORE IMPORTANT ELEMENTS [1]

	VALENCE	MILLIGRAMS DE- POSITED BY 1 AM- PERE IN 1 SECOND	GRAMS DEPOSITED BY 1 AMPERE IN 1 HOUR
Aluminum . . . . . Al	3	0.0936	0.337
Antimony . . . . . Sb	3	0.4152	1.495
Arsenic . . . . . As	3	0.2590	0.9323
Barium . . . . . . Ba	2	0.71175	2.5623
Bismuth . . . . . . Bi	4	0.5414	1.949
Bromine . . . . . . Br	1	0.8282	2.981
Cadmium . . . . . . Cd	2	0.5824	2.096
Calcium . . . . . . Ca	2	0.2076	0.7476
Cerium . . . . . . Ce	3	0.4845	1.7440
Chlorine Cl	1	0.3675	1.3228
Chromium . . . . . Cr	2	0.2694	0.970
Chromium . . . . . Cr	3	0.1796	0.647
Cobalt . . . . Co	2	0.3055	1.0999
Cobalt . . . . Co	3	0.2037	0.7333
Copper . . . . Cu	1	0.6588	2.3715
Copper . . . . . . Cu	2	0.3295	1.1857
Fluorine . . . . . . Fl	1	0.1969	0.709
Gold . . . . Au	1	2.045	7.360
Gold . . . . Au	3	0.6815	2.453
Hydrogen . . . . . H	1	0.01045	0.03704
Iodine I	1	1.3152	4.7347
Iron . . . . Fe	2	0.2893	1.0416
Iron . . . . Fe	3	0.1929	0.6944
Lead . . . . Pb	2	1.0737	3.8648

[1] Based on the atomic weights given above and on the value 96,500 for the electrochemical constant.

TABLE OF ELECTROCHEMICAL EQUIVALENTS — *Continued*

	VALENCE	MILLIGRAMS DE-POSITED BY 1 AMPERE IN 1 SECOND	GRAMS DEPOSITED BY 1 AMPERE IN 1 HOUR
Lithium Li	1	0.0719	0.259
Magnesium . . . . . Mg	2	0.1260	0.4536
Manganese . . . . . Mn	2	0.28462	1.0246
Manganese . . . . . Mn	3	0.18974	0.68307
Mercury . . . . . . Hg	1	2.079	7.483
Nickel . . . . Ni	2	0.3040	1.093
Nickel . . . . Ni	3	0.2027	0.7297
Oxygen . . . . . . O	2	0.08290	0.2984
Potassium . . . . . K	1	0.4052	1.4586
Silver . . . . Ag	1	1.1180	4.0242
Sodium . . . . . . Na	1	0.2383	0.8580
Tin . . . . Sn	2	0.6150	2.214
Tin . . . . Sn	4	0.3075	1.107
Titanium . . . . . . Ti	4	0.1246	0.4486
Tungsten . . . . . W	6	0.318	1.144
Zinc . . . . Zn	2	0.3387	1.2193
Zirconium . . . . . Zr	4	0.2347	0.845

NUMERICAL RELATION BETWEEN VARIOUS UNITS

ENGLISH AND METRIC MEASURES

NOTE. — Values taken from "Tables of Weights and Measures," U. S. Coast and Geodetic Survey, 1890.

LENGTH

1 meter = 39.37 inches (legalized ratio for the U. S.)
1 meter = 1.093611 yards
1 meter = 3.280833 feet
1 kilometer = 0.621370 mile
1 inch = 25.40005 millimeters
1 foot = 0.304801 meter
1 yard = 0.914402 meter
1 mile = 1.609347 kilometer

MASS

1 kilogram = 2.204622 pounds av.
1 gram = 15.43235639 grains
1 pound = 0.4535924277 kilogram
1 ounce av. = 28.34853 grams
1 ounce troy = 31.10348 grams
1 metric ton = 1000 kilograms

VOLUME

1 liter = 1.05668 quarts
1 liter = 0.26417 U. S. gallon
1 liter = 33.814 U. S. fluid ounces
1 quart, U. S. = 0.94636 liter
1 gallon, U. S. = 3.78544 liters
1 fluid ounce = 0.029573 liter

UNITS AND CONVERSION FACTORS

(From Pender's *Handbook for Electrical Engineers*, 2d ed., 1922)

1 kg.-cal. = 3.968 B.t.u. = 4183 joules = 426.6 kg.-meters
1 joule = 10^7 ergs = 0.2390 gram-cal.
1 horse power = 0.7457 kw. = 1.014 metric h.p.

LEGAL ELECTRICAL UNITS [1]

The legal electrical units in the United States are defined as follows:

(1) The unit of resistance is the international ohm, represented by the resistance offered to a steady current by a column of mercury at 0° C. whose mass is 14.4521 grams, of a constant cross-section, and whose length is 106.3 centimeters.

(2) The unit of current is the international ampere and is the equivalent of the unvarying current, which, when passed through a solution of silver nitrate in water, in accordance with standard specifications, deposits silver at the rate of 0.001118 gram per second. See p. 7 for the method of making measurements.

(3) The unit of electromotive force is the international volt, which is the electromotive force that, steadily applied to a conductor whose resistance is one international ohm, will produce a current of an international ampere and is practically equivalent to $\frac{1}{1.434}$ of the electromotive force of a Clark cell, at 15° C., when prepared according to the standard specifications.[2]

(4) The unit of quantity is the international coulomb, which is the quantity of electricity transferred by a current of one international ampere in one second.

(5) The unit of work is the joule, equal to 10^7 ergs, and is practically equivalent to the energy expended in one second by an international ampere in an international ohm.

(6) The unit of power is the watt, and is practically equivalent to the work done at the rate of one joule per second.

[1] Bulletin of U. S. Coast and Geodetic Survey, Dec. 27, 1893.
[2] See Bulletin of U. S. Coast and Geodetic Survey, Dec. 27, 1893. Later experiments gave an e.m.f. of 1.4328. See Pender's *Handbook for Electrical Engineers*, p. 187 (1922).

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